Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 195 JANUARY, 1923 No. 1

RECENT ADVANCES IN PHOTOGRAPHIC THEORY.*

BY

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A PAPER, which was presented to The Franklin Institute in 1920, dealt with the structure of the photographic image and, incidentally, with the structure of unexposed photographic materials. Since that time, the structure of the sensitive material itself has been investigated by a number of workers, and the work has proved most fruitful in the increase of our knowledge of the properties and behavior of photographic sensitive materials. Already much light has been thrown on the nature of sensitiveness itself and on the behavior of the silver salts when they are acted upon by light.[1]

One of the greatest problems in all photographic science is the theory of emulsion making; that is, the discovery of the systematic relations which must exist between the methods employed in the preparation of the emulsion and the photographic properties of the material obtained. Attempts to solve this problem have

* Presented at a joint meeting of the Sections of Physics and Chemistry and Photography and Microscopy held Thursday, December 7, 1922. Published as Communication No. 165 from the Research Laboratory of the Eastman Kodak Company.

[1] A review of the present state of the subject, dealt with in this lecture, has recently been published in the JOUR. FRANK. INST., by Wightman, Trivelli and Sheppard ("Studies in Photographic Sensitivity," JOUR. FRANK. INST., **194**, 1922, p. 485) and I am indebted to them for many suggestions incorporated here.

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led to the subdivision of the subject into three separate studies: (1) The physico-chemical relations between the concentration, temperature, and other conditions existing during emulsion making, and the nature of the precipitate obtained; (2) the analysis of the precipitate into grains of different sizes; (3) the correlation of the frequency curves for the size of the grains of the emulsion with the photographic properties of the emulsion itself. Work on all three branches of the problem is now well under way.

The study of the physico-chemical relations on which depend the form in which a precipitate is produced has been developed by a number of workers in recent years, and its application to the precipitation of silver halide has been studied by Trivelli and Sheppard, their work being published in a monograph on the silver bromide grain.[2]. In the course of this paper, it is desired to present some of the results which have been obtained in connection with the analysis of the different sizes of grain which occur in emulsions. The correlation of the frequency curves with the photographic properties of the emulsion itself has already been dealt with by Wightman, Trivelli, and Sheppard, and will probably not present much difficulty when the nature of the frequency curve is more fully understood, and we may therefore expect that before long we may be able to define the form of the precipitate of silver bromide which will produce given photographic properties in the emulsion. An effective control of emulsion making will, of course, involve much study of the conditions of precipitation and also of the properties of the gelatine, which, apparently, has a very great influence on the specific sensitiveness of the silver halide produced.

For many years the nature of the product of light action upon silver halide, which is generally known as the "latent image," has been the subject of speculation and discussion, but the work which has been done upon the individual grains which compose the sensitive surface of a photographic material enables the nature of the latent image and its production to be attacked from a new angle, which must be valuable in shedding light upon this classical problem. The chief workers in this field are in three different countries. Professor The Svedberg, of the University of

[2] Trivelli, A. P. H., and Sheppard, S. E., "The Silver Bromide Grain of Phot. Emulsions," Eastman Kodak Company, Rochester, N. Y.

Upsala, Sweden, published the first paper in 1919.[3] This dealt specifically with the influence of the grain structure upon sensitiveness. In 1918, there was formed in England a research association for the photographic industry, the first director of which was R. E. Slade. He and his colleagues, G. I. Higson and, later, F. C. Toy and W. Clark, have published a number of papers on the subject.[4] In the research laboratory of the Eastman Kodak Company, when Svedberg's paper appeared, A. P. H. Trivelli[5] had already been at work for some time studying the microscopic structure of emulsions, and with his colleague F. L. Righter has now published several papers. At the same time E. P. Wightman and S. E. Sheppard[6] have attacked the problem and within the last two years L. Silberstein[7] has done a great deal of work on the mathematical analysis of the questions involved.

In his earlier work Trivelli made a large number of photomicrographs of emulsions taken from standard photographic plates and films, one of which is reproduced in Fig. 1.

It will be seen that the silver bromide grains, of which the emulsion is composed, are of extremely varied sizes, there being present a large number of small grains, down to the limit of those visible with a microscope, and a smaller number of large grains, including some of very much greater area than the smallest grains present. The largest grains are all polygons with angles of 60° and 120°. There is a tendency to round off the corners and edges of the small grains, so that the smallest grains appear to be more or less spherical.

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[3] Svedberg, The, "Körngrosse und Empfindlichkeit in Photographischen Emulsionen," *Z. Wiss. Phot.*, **20**, 1920, p. 36.

[4] Slade, R. E., and Higson, G. I., "Photochemical Investigations of the Photographic Plate," *Proc. Roy. Soc.*, **98A**, 1920, p. 154.

Higson, G. I., "The Action of Light on the Photographic Plate," *Phot. J.*, **45**, 1921, pp. 35, 144.

Toy, F. C., "The Sensitivity of Silver Halide Crystals which are Geometrically Identical," *Phot. J.*, **45**, 1921, p. 471.

[5] Sheppard, S. E., and Trivelli, A. P. H., "Note on the Relation between Sensitiveness and Size of Grain in Photographic Emulsions," *Phot. J.*, **45**, 1921, p. 400.

[6] Wightman, E. P., and Sheppard, S. E., "Size-Frequency Distribution of Particles of Silver Halide in Photographic Emulsions and its Relation to Sensitometric Characteristics, I and II," *J. Phys. Chem.*, **25**, 1921, pp. 181, 561.

[7] Silberstein, L., "A Quantum Theory of Photographic Exposure," Part I, *Phil. Mag.*, **44**, 1922, p. 257.

A study of these small spherical grains by R. B. Wilsey,[8] however, using the methods of X-ray crystal analysis, shows that even the smallest grains are still definitely crystalline and have the same structure as the large grains, the crystalline form being a cubic lattice. The shape of the large grains is very well illustrated in Fig. 2, which shows a special emulsion prepared to give a large proportion of relatively large grains.

The fact that the grains in an emulsion are of many different sizes has been known for many years, and in 1915 in a paper presented to The Franklin Institute entitled "The Physics of the Photographic Process," [9] attention was called to the fact that the sensitiveness will depend upon the distribution of different sizes of grains, as will also the shape of the plate curve, this curve being the relation between density and logarithmic exposure. It was suggested that the shape of the curve will depend to a considerable extent on the distribution of the different sizes of grains in the emulsion. With a homogeneous emulsion we shall have a curve with a short over- and under-exposure portion, as seen in Fig. 3, and by adjusting the sizes of grains so that there is a sufficient number of grains distributed around the mean, we can diminish the under-exposure portion to obtain a longer straight line (Fig. 4). We can therefore form a mental picture of the relation between the distribution of the grain and the sensitiveness curve.

It will be seen from this that as long ago as 1915 it was realized that the distribution of the different sizes of grains in an emulsion might play a very important part in determining the characteristics of that emulsion. The problem was to measure the distribution of the grains; that is, the number of grains of a given size which occurred in an emulsion and the variation of the number with the size of the grain. This is a problem which has often arisen in scientific work. It has been studied in connection with suspensions of all kinds.[10] Various indirect methods of attacking the problem have been suggested. It is possible to get determinations by settling the emulsion, taking advantage of the fact that the larger particles will settle most rapidly according to Stokes' law.

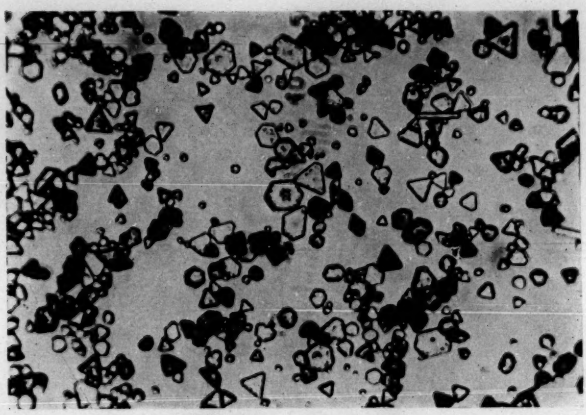
[8] Wilsey, R. B., "The Crystal Structure of Halides," *Phil. Mag.*, **42**, 1921, p. 262.

[9] J. FRANK. INST., 179, 1915, p. 141.

[10] "A Photomicrographic Method for Det. of Particle Size of Paint and Rubber Pigments" by Henry Green, N. J. Zinc Co., J. FRANK. INST., Vol. 192, Nov., 1921, p. 637.

This has been carried out in various ways by Odén, Westgren, and others,[11] but the direct method is, clearly, to spread out a thin layer of the emulsion and to count the different sizes of grains occurring in it. Trivelli accomplished this by photomicrographic methods. He photomicrographed a thinly coated emulsion at an enlargement of 2500 diameters, enlarged the negatives to 10,000 diameters, outlined all the grains of these enlargements, and then planimetered the grains and obtained tables showing the areas

FIG. 1.



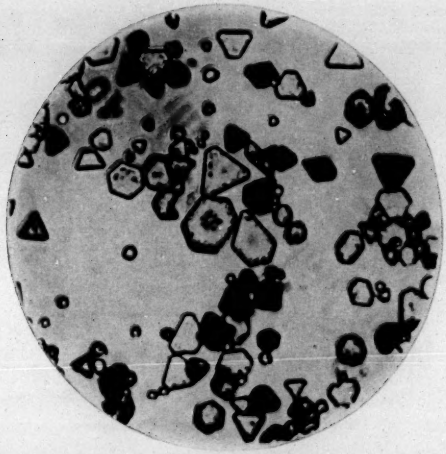
Silver halide grains of a photographic emulsion.

of the different grains present, at least a thousand grains being counted for each emulsion. Wightman and Sheppard obtained the same results by the use of the camera lucida instead of photomicrography. From the tables, curves were obtained showing the relation between the size of grains and the number present for several standard emulsions. Fig. 5 shows the results for the portrait film and slow lantern emulsions: It will be seen that the curve for portrait film shows a distribution of sizes of grain which corresponds approximately to a probability curve, the maximum number

[11] Odén, S., *Intern. Mitt. und Bodenkunde*, **5**, 1915, p. 257; *Proc. Roy. Soc.*, Edinburgh, **36**, 1915–16, p. 219; *Koll. Zeit.*, **18**, 1916, p. 33; **26**, 1920, p. 100.
Westgren, A., *Zeit. Anorg. Chem.*, **94**, 1916, p. 193.

of particles being for particles of a diameter of approximately 0.5μ, the particles both smaller and larger than this being fewer, until we have very few particles indeed of larger size than 2.7μ and also few of smaller size than 0.2μ. On this small side no particles can be measured less than 0.2μ because this is the limit of the resolving power of the microscope, so that even if smaller particles exist, as they certainly do in some emulsions, they cannot be measured. Sometimes the maximum number of particles are

FIG. 2.



Silver halide grains of large size from a special emulsion.

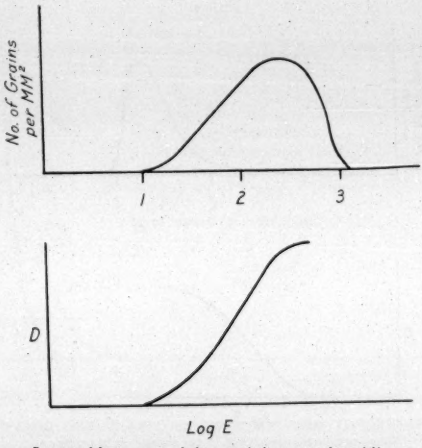
those of very small size, and in this case the maximum is so far on the small side that no maximum can be measured owing to the limit of the resolving power of the microscope, and, instead of a symmetrical probability curve, we get one of an exponential shape. This is shown in the curve of the lantern slide emulsion.

It is probable, however, that curves showing diameters will not be those of real value, because the controlling factor will not be the diameter of the particles, but their projective area, and the factor of importance in relation to their projective area is not the number, but the effective area of the particles of a given area

size, so that instead of using curves in which the number of particles are plotted against the diameter, we should rather use those in which the effective projective area of the grains of a given size is plotted against the area of the single grains; the curves for the two emulsions previously referred to are given in Fig. 6.

While this work was in progress, Slade and Higson [12] had studied the grain of process plates, which they thought to be very homogeneous in size, and they considered that if the grains are all

FIG. 3.



Suggested frequency and characteristic curves of emulsion.

of the same size, we get the steepest characteristic curve possible, while if the grains are not all of one size a flatter curve is obtained. They found that, in all the cases they examined, the steepness of the curve could be foretold from the photomicrographs.

Svedberg [13] investigated systematically the relation between the size and sensitiveness of grains in photographic emulsions.

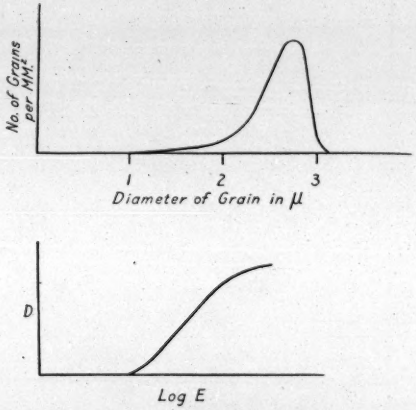
[12] Slade, R. E., and Higson, G. I., "The Emulsion for a Process Plate," *Phot. J.*, **43**, 1919, p. 260.

[13] Svedberg, The, and Anderson, H., "On the Relation between Sensitiveness and Size of Grain in Photographic Emulsions," *Phot. J.*, **45**, 1921, p. 325.

Svedberg, The, "The Reducibility of the Individual Halide Grains in a Photographic Emulsion," *Phot. J.*, **46**, 1922, p. 183.

He prepared emulsions so thinly coated that the grains were all in single layers and counted the grains of different sizes by classifying them into four classes. The emulsions were then exposed and developed and the developed silver removed, the remaining grains, representing those which had not been made developable by the action of light, being counted. In this way curves could be obtained showing the sensitiveness of the grains of each class, and it was found, as might be expected, that the larger grains were much more sensitive than the smaller grains.

FIG. 4.



Suggested characteristic and frequency curves of emulsion.

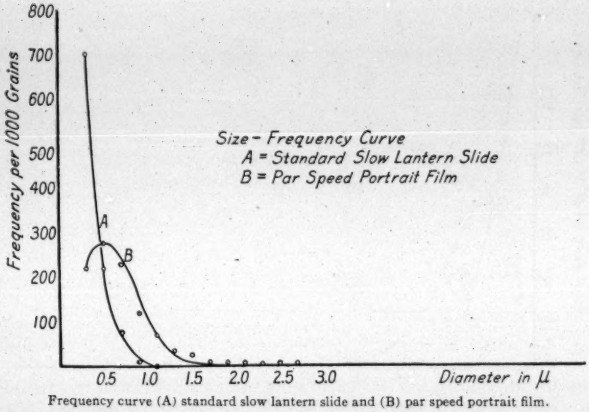
Svedberg [14] next suggested that the product of the light action in the halide grain, that is, the substance of the latent image, consists of small centres distributed through the grain or through the light affected part of the grain, and that these centres are distributed according to the laws of chance. A certain grain will therefore become developable if it includes one or more developable centres after exposure, and, according to the laws of chance, the probability of centres occurring in a grain can be calculated. The centres become visible during development, for if a plate be developed for a very short time, the grains show these centres as

[14] Svedberg, The, "On the Relation between Sensitiveness and Size of Grains in Photographic Emulsions," *Phot. J.*, **46**, 1922, p. 186.

small black spots upon them. This was shown by Hodgson [15] as early as 1917 (Fig. 7).

Svedberg showed the centres clearly and made plain their relation to the silver bromide grains by photographing the grains before development by deep red light, then developing for a short time, and removing the undeveloped halide. On the plate, there are then left small dots, and comparison with the first plate showed these to correspond with the silver halide grains originally present.

FIG. 5.



Frequency curve (A) standard slow lantern slide and (B) par speed portrait film.

Fig. 8 showing this is reproduced here from Svedberg's paper.[16] In the figure, *A* represents the undeveloped silver halide grains and *B* the centres found after removal of the grains. In *C* the two figures are shown superimposed so that the centres are shown on a faint outline of the original grain.

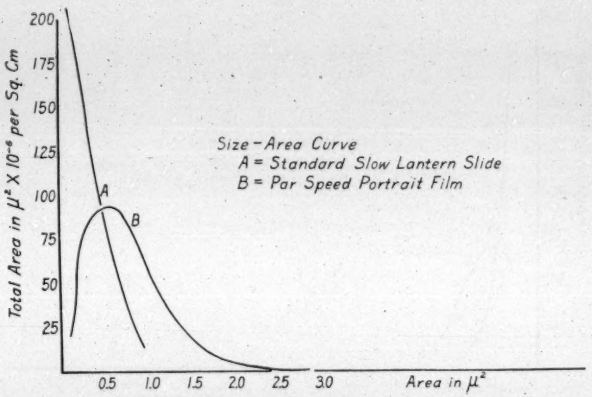
Svedberg has shown that the number of centres produced in this way by initial development increases with the exposure in accordance with the usual photographic laws, and it might be assumed that the discovery of these centres produced during development is a proof of discreteness in the action of light upon

[15] Hodgson, M. B., "Physical Characteristics of the Elementary Grains of a Photographic Plate," J. FRANK. INST., **184**, 1917, p. 705.

[16] Svedberg, The, "The Interpretation of Light Sensitivity in Photography," *Phot. J.*, **46**, 1922, p. 310.

the grain and that they must result from a structure in the silver bromide grains either existing before exposure or produced during exposure and corresponding, for instance, to spots of sensitiveness. While the evidence for this seems very great, it must be remembered that we know nothing about these centres until development takes place and that even if the whole grain were equally affected by the action of light and changed to the same extent, we should still expect development to take place first at

FIG. 6.



Size-area curve (A) standard slow lantern slide and (B) par speed portrait film.

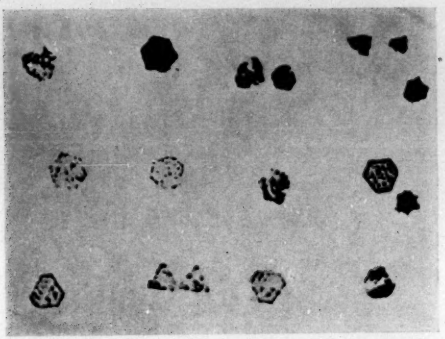
some local spot corresponding to slight surface differences in the grain. A sheet of metal immersed in acid, for instance, will not be attacked uniformly all over the surface. Because of the impurities, action will start at individual points, and since development corresponds presumably to deposition of silver from a supersaturated solution, it would naturally occur at local spots if any form of impurity were present and would proceed first at those spots. It may be argued that the presence of such impurities in the grain would of itself produce changes in sensitiveness, but the point that it is wished to emphasize is that local initial development is not necessarily associated with local differences of sensitiveness.

In his work on silver halide grains, Trivelli showed by his photomicrographs distinct spots of reduction produced by the

action of light before any development had been applied to the grains (Fig. 9).

On development, however, he found that the centres of reduction produced at the beginning of development did not correspond to the visibly affected spots which were produced by the action of light. These spots were distributed over the surface of the grain, whereas the initial reduction most frequently started at the edges or corners of the grain. The fact that the

FIG. 7.



Partly developed grains showing centres.

centres of development start at the edges of the grain is mentioned also by Toy [17] and is, of course, in accordance with what one would expect for a reaction such as development, if the edges and corners have a greater solution pressure than the rest of the surface, and thus these will be more liable to attack.

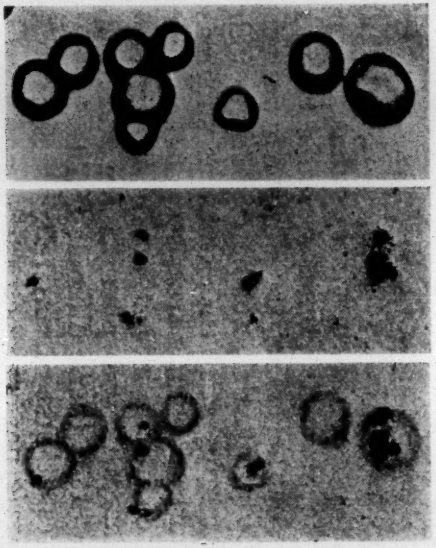
If we assume that developable centres correspond to a segregation of the latent image, then the distribution of centres according to a probability law is what we should expect, however they are produced, since a chance distribution would be most probable in the absence of any known cause leading to another specific distribution.[18]

[17] Toy, F. C., "The Quantum Theory of Photographic Exposure: A Criticism," *B. J.*, **69**, 1922, p. 443; "On the Theory of the Characteristic Curve of a Photographic Emulsion," *Phil. Mag.*, **44**, 1922, p. 352.

[18] Cf. Toy, F. C., *Phil. Mag.*, 1922, p. 354, and Wightman, Trivelli and Sheppard, *loc. cit.*

In a recent paper, W. Clark [19] of the British Photographic Research Association has acted upon grains with a reducing solution such as sodium arsenite and concludes from his results that the centres are an essential part of the grain structure and they exist in the grains from the time the emulsion is made. The

FIG. 8.



Grains and development centres.

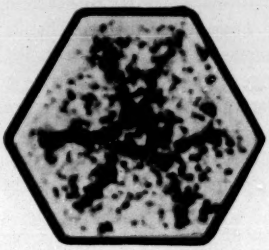
validity of Clark's conclusions depends upon the assumption that the centres are not produced during development but exist before it, and the fact that he gets exactly the same chance distribution by the action of sodium arsenite as for light would suggest either that the centres attacked by light are also attacked by sodium arsenite or that the centres produced on development are produced

[19] Clark, W., "Grain Structure *versus* Light Quanta in the Theory of Development," *B. J.*, **69**, 1922, p. 462.

by development and are not directly dependent upon the existence of localized changes before development.

In the very important paper by Toy, quoted above, measurements are given showing that the number of nuclei produced on initial development are proportional to the number of grains which become developable on complete development and that the larger grains not only have more nuclei on account of their size, but that these nuclei are more sensitive to light than those in the smaller grains, the sensitivity of a grain being the sensitivity of its most sensitive nucleus. Svedberg considers that the number

FIG. 9.



A silver bromide crystal deposited from solution in ammonia showing surface decomposition produced by light.

of developable centres per unit area of grain surface is a measure of the light sensitivity of the silver halide of the emulsion. From Toy's work it would seem to be doubtful whether we can speak of the light sensitivity of the halide itself in terms of the nucleus theory, since this will vary with the size of the grain.

As will be shown later, Silberstein has come to much the same conclusion as Svedberg as to the relation of the number of developable centres to light sensitivity and has given mathematical formulæ for this connection.[20]

Renwick [21] has suggested that sensitiveness is due to nuclei which probably consist of a colloidal solution of silver in the halide. He thinks that in the crystalline silver bromide there is

[20] Silberstein, L., "A Quantum Theory of Photographic Exposure," Part III, to be published shortly in *Phil. Mag.*

[21] Renwick, F. F., "Colloid Chemistry and Photography," *B. J.*, **68**, 1921, p. 607.

present some highly unstable form of colloid silver in solid solution, and it is this colloid silver which first undergoes change on exposure to light. He believes that these silver particles may be negatively charged and that the action of light is to discharge them and thus enable the coagulation into larger groups of the particles of colloidal silver which existed in the grain before exposure. He believes that it is these groups of coagulated particles which are the reduction centres.

While Svedberg was studying the distribution of the developed centres among the grains and finding that they had a probability distribution, Silberstein and Trivelli [22] made the same discovery for the number of grains which become developable with a given time of exposure. They found that the chance of a grain becoming developable increased very much with its size and obtained an equation leading to the same results as Svedberg's for the relation between the number of developable grains and their area. Silberstein, however, who obtained his formula theoretically before the experiments of Trivelli were completed, ascribed this not to structure in the material, but to a structure in the radiation falling upon it.

Recently, a number of phenomena have been observed which are very difficult to explain by the use of the classical wave theory of light, and it seems not unlikely that it may be necessary to turn to a theory having some analogy to the corpuscular theory. As a first step towards this, Max Planck suggested his now well-known quantum hypothesis, according to which an atom radiating energy liberates it in discrete quanta, the amount of energy corresponding to each quantum being a constant multiplied by the frequency of the light. Bohr adopted Rutherford's theory of the structure of the atom, considering the atom to consist of a nucleus carrying a positive charge of electricity and to be surrounded by one or more electrons carrying a negative charge, the electrons revolving about the positive nucleus itself. He imagined that the electrons revolve without radiating but that when an electron suffers some violent shock, it gives energy, and that this energy is radiated and has the value of Planck's quantum.

[22] Silberstein, L., "Quantum Theory," Part I, *loc. cit.*

Trivelli, A. P. H., and Righter, F. L., "A Preliminary Investigation on Silberstein's Quantum Theory of Exposure," *Phil. Mag.*, **44**, 1922, p. 252.

Thus, if an electron, by the sudden impact of another electron, for instance, is thrown out of an atom and is attracted back to its place by the nucleus, then as it falls back, it will send out a pulse of energy, and it will be seen at once that if light is produced by such a behavior of electrons, it is inherently probable that it will be radiated in pulses rather than continuously. Since, according to Bohr, the frequency of the vibration emitted is exactly proportional to the energy which the electron releases, Planck's quantum condition is fulfilled, and we have the famous equation

$$Ve = h\nu$$

where

V is the voltage acting on the electron charge e
ν is the frequency

and

h is Planck's constant

In an X-ray tube, the discharge of electricity is in the form of a stream of corpuscles travelling with a velocity which is very high and which depends upon the voltage of the electric current applied to the tube. When these corpuscles strike the target, their energy is radiated in the form of X-rays, and we know that these X-rays partake very closely of the nature of light except that the length of the waves is about one-thousandth of those of light or, what is the same thing, their frequency is a thousand times as great. It is to this that they owe their great penetrating power.

On the classical wave theory of light, then, we should imagine that an X-ray tube having its target bombarded by the stream of corpuscles produced by the current would emit waves of X-rays spreading into space just as waves of light are imagined to spread from a source; but now comes a great difficulty. When these X-ray waves travelling out pass through a gas and are absorbed, they cause the molecules of the gas to emit electrons, and these electrons are emitted with almost exactly the same velocity as the electrons in the tube which produced the X-rays themselves. The extraordinary nature of this phenomenon is well illustrated by Sir William Bragg in a recent article:[23] He takes as an analogy the dropping of a log of wood into the sea from a height of one hundred feet. A wave radiates away from where it falls; the wave spreads; its energy is more and more widely distributed;

[23] Bragg, W., "Electrons and Ether Waves," *Sci. Monthly*, **14**, 1922, p. 153.

the ripples die away; at a short distance, a few hundred yards perhaps, the effect will apparently disappear. If the water were perfectly free from viscosity, and there were no other causes to fritter away the energy of the waves, they would travel indefinitely, always diminishing in their height. Now, at some point, say a thousand miles away, these now microscopic ripples encounter a wooden ship. We should expect that they would produce no effect, especially as they may have passed many other ships without having affected them, but, for some reason, as these tiny ripples reach the ship, a plank of the same weight as the log is hurled out of the ship to a height of exactly one hundred feet, and the whole energy which was originally supplied by the log falling into the water is concentrated upon the ejection of the plank. It will be seen at once how inadequate the wave theory is to account for this phenomenon. Similar difficulties occur in connection with photoelectricity or the liberation of electrons under the influence of light.

The method by which a photographic emulsion adds up light during a long exposure has always been a great problem when it is considered from the standpoint of the classical wave theory. If we accept the idea that the grains of silver halide in an emulsion are exposed to a continuous flood of light from a distant star, for instance, then each grain must be imagined to be integrating light until it has received enough to make it developable. Since the exposure required in astronomical photography is frequently very long, we must consider that the grains continue to integrate the light for many hours, and it is difficult to imagine any mechanism which would enable them to do this. The difficulty is enhanced by the fact that even a very brief exposure continues to produce an effect after an interruption of a long period, so that if all the grains have been affected by the first exposure, they must be capable of storing energy quite insufficient to make them developable and to hold this energy for a long period and then resume its accumulation at the level where the interruption occurs. In the same way, when we study the exposure of the individual grains, even if we could imagine some mechanism by which the grains could store up the energy falling upon them until they became developable, we should expect that all the grains of the same size would become developable at the same time unless, indeed, we assume the process of exposure to be

autocatalytic in nature. When grains are examined under the microscope, however, some of them are found to have been affected before others. If we imagine that they all have become exposed to a uniform flood of light, we must consider that these grains differ in sensitiveness among themselves and that the possibility of change on exposure, so that they become developable, is due to the presence of a sensitizer. This may either be concentrated unequally in the different grains or may form centres of sensitiveness similar to those supposed to exist by Svedberg and other workers in the field who think that the centres found at the beginning of development are the origin of sensitiveness and are present from the time of making the emulsion.

If we had no prior knowledge of the wave theory of light, however, it is clear that the simplest explanation of the sensitiveness of different grains would be that, instead of a continuous flow of light in the form of waves on to sensitive films, the light was falling upon it as a rain of projectiles and that these projectiles made developable any grains that they hit, the grains that were missed not being developable but being hit later if they continued to be exposed to the radiation. Naturally, the bigger the grains, the more likely are they to be hit, so that a calculation can be made of the relation between the size and the percentage number of grains which will become developable after a given exposure.

When this was tested experimentally, it was found that in the plates which were used in which the grains are spread out in a single thin layer, the grains tended to stick together in clumps, two or three small grains attaching to each other, and it was found experimentally that if one of these grains is affected by light, the whole clump becomes developable. The developability of a clump by infection from a single exposed grain has been questioned. Svedberg examined this subject for his own plates and found specifically that no such infection occurred. On the other hand, Trivelli and Righter measured many clumps on their plates and considered the existence of infection to be proved beyond doubt.[24] It is quite probable that the discrepancies are due to differences in

[24] Trivelli, A. P. H., Righter, F. L., and Sheppard, S. E., "On the Mutual Infection of Contiguous Silver Halide in Photographic Emulsions," *Phot. J.*, **46**, 1922, p. 407.

the emulsion. Trivelli has found in recent work [25] that different preparations of an emulsion show great differences in the tendency of clumps to become infected, some preparations showing a large proportion of clumps which are entirely developable, while in other preparations it is quite possible to develop one grain of an apparent clump and to have other grains showing no development.

On any chemical theory of differences of sensitiveness in the grains, it is difficult to imagine that a clump of grains will be more sensitive than the most sensitive single grains, although we could imagine that a big grain would be more sensitive than a smaller grain, but on a light projectile theory, a clump of small grains will act just as if it were one big grain of the same area, because the chance of one of the grains being hit by a light projectile and making all of them developable is just the same as if the total area were filled by one grain. It is consequently possible to calculate the rate at which clumps containing different numbers of grains will be affected by the light, and when this was measured experimentally for clumps containing two, three, four, and more grains, it was found that the values of "sensitiveness" of the different clumps agree very well with those which were calculated on the light projectile theory as developed by Silberstein.

Whatever the projectile of light is, it must be associated in some way with waves, because, as was said earlier, the frequency of the vibration emitted is proportional to the energy of the electron which produced it, and so, while we have gone back to a projectile theory of light, instead of the idea of a continuous wave front, we have not abandoned waves. Silberstein suggests that the projectiles rather than being called "corpuscles," which gives the idea that they are round, should be called "light darts" and should be imagined to consist of a long train of waves of very small diameter travelling with the velocity of light.

Einstein has found that the emission of energy from an atom emitting its spectral radiation must be definitely oriented in direction and cannot be propagated in a spherical wave, the atom recoiling and thus preserving the thermodynamic equilibrium.

It is obvious that this theory of light darts would meet the difficulties which are offered by the phenomena of X-rays and photoelectricity to the idea of a continuous wave front, while not

[25] A letter on "The Effect of Development upon Grain Clumps," *B. J.*, 69, 1922, p. 687.

excluding the possibility of the formation of interference and diffraction effects, and at first sight it would seem to offer a solution of the problem of the integration of exposure by the silver halide grains of the emulsion, since we might assume that instead of a grain integrating energy falling upon it until it had received enough to make it developable, it was not affected at all until struck by a quantum of light and then became developable completely. If this were so, however, we should expect that the amount of energy necessary to make a grain developable would be, on the average one, and at most, a few quanta, more than one being necessary because of the chance that a fresh grain would not be struck by every "light dart" falling upon the emulsion, some falling between the grains and others striking grains which were already developable.

It has long been known that the amount of energy required to make a grain developable is in absolute amount very small, and in my paper before the Institute in 1915 it was suggested that quite possibly it was of the order of one quantum per grain, this being derived from a rough calculation by P. G. Nutting based on some measurements of the energy required to make a plate developable to a given density.

Up to the present there have been very few trustworthy measurements of the amount of energy necessary to make photographic plates developable, and the measurements available are not in such a form that a satisfactory factor for the number of developable grains after exposure can be found. Leimbach [26] made a number of careful measurements of the energy transmitted through a monochromatic spectrophotometer. He found that for a Schleussner plate 0.6 erg per square centimetre would give a density of unity at a wave-length of 450$\mu\mu$. In some work which has just been started in our laboratory we are getting results of the same order as those of Leimbach, and I think we may conclude as a preliminary statement that for high-speed emulsions several hundred quanta of violet light are necessary per grain in order to make the grain developable.

If this result is confirmed, the light dart hypothesis would scarcely seem to be sufficient by itself to explain the integration of energy by the emulsion, and we are thrown back on to the idea of differential sensitiveness among the grains or of spots of

[26] *Zeit. Wiss. Phot.*, Vol. 7, No. 5, pp. 157 and 181; *Sci. Abs.*, Vol. 12, p. 1209.

limited area on the grains, so that of the hundreds of quanta striking a grain only one may be considered to be operative, the rest falling upon the insensitive portions of the grain. Suppose that the fraction of a grain which is sensitive is ε and this consists on an average of $\overline{K}$ spots of ω area; then,

$$\overline{K}\omega = \varepsilon a.$$

Now, if a grain has no spots it will be quite insensitive and will not be developable no matter how long it is exposed, so that the value of $\overline{K}$ and ω can be determined experimentally by counting the grains left over after a very prolonged exposure.

The distribution of sensitiveness among the grains of an emulsion may thus be ascribed to (1) a heterogeneity in the radiation, together with a variation of sensitiveness either over the whole surface or in the form of local centres in the material, in which case the sensitiveness will be a probability function of the size of the grain, or (2) a distribution of centres of sensitiveness, which will also be distributed according to a probability function. This function may either be proportional to the volume or to the area of the grain, while the chance of being hit by a light dart would be proportional to the area only. It seems to be possible that no crucial distinction between the two hypotheses can be made by direct photographic determinations. A study, however, of the effect of desensitizers upon the developability of grains exposed to light may make a decision possible. In any case, a question of great importance in connection with the latent image is the amount of energy required to make the silver halide developable. If the new determinations show that several hundred quanta of violet light per grain are necessary, then a revision of ideas relating to the latent image itself will follow as compared with those ideas derived from the belief that the energy available is only one quantum per grain, in which case it is clear that the latent image must depend upon a change occurring in a single atom of silver or halogen, since the only work we can imagine one quantum capable of doing to be the release of a single electron from an atom. If several hundred quanta per grain are available, then it is clear that not one atom of silver per grain may be affected but that several hundred atoms may be changed and that an appreciable, though very small, amount of chemical decomposition may be effected by the energy available. More important

still, quantitative differences in the amount of latent image present in a grain become possible. If only one quantum per grain is available, a grain is either exposed or not exposed, but if energy corresponding to an amount of several hundred quanta are used, we might imagine that a grain could become partly exposed, so that, for instance, it might be developable by a developer of high reduction potential but not by one of low reduction potential. Moreover, grains might clearly be of different degrees of sensitiveness, that is, they might require different amounts of energy to make them developable, and the whole idea of quantitative differences in sensitiveness and exposure, which is so difficult if we imagine one quantum of energy per grain to be sufficient to produce a complete change in the grain which will make it developable, becomes perfectly intelligible. On the other hand, the division of the sensitive area into a number of small sensitive spots, which accords with the ideas both of Silberstein and of those other workers such as Svedberg who have located sensitiveness in "centres," would still enable us to retain the idea that a single quantum of energy is sufficient for exposure if it reaches one sensitive spot.

In concluding this paper I feel that my presentation of the subject demands some apology. I have endeavored to summarize the recent work done by a number of workers on the theory of photographic sensitiveness, but I have not been able to present a clear and definite creed drawn from their findings. The facts which have been ascertained are not as yet sufficiently coördinated to enable us to distinguish between the several explanations which are possible and I have chosen rather to put forward, as fairly as I can, the views held by others, than to select one specific theory and advocate its adoption. The work of the next few years will undoubtedly clear up much that is dark and uncertain at the present time.

Spontaneous Decomposition of Ammonium Chlorate.—According to FRED FAIRBROTHER, of Victoria University, Manchester, England (*Jour. Amer. Chem. Soc.*, 1922, xliv, 2419–2422), the rate of the spontaneous decomposition of ammonium chlorate is autocatalytically accelerated when the products of the decomposition are not quickly removed. The solid mass, which remains at the end of the reaction, is almost pure ammonium nitrate, and is free from chlorides. J. S. H.

The Relation between the Evolution of Heat and the Supply of Energy during the Passage of an Electric Discharge through Hydrogen. J. KEITH ROBERTS. (*Proc. Roy. Soc.*, A 714.)—"In this paper an account is given of measurements of the heat evolved by the passage of a known current under a known potential through a hydrogen discharge tube. The experiment was suggested by Sir Ernest Rutherford as a possible test of the hypothesis in which he supposed that a much closer combination between an electron and a hydrogen nucleus than that existing in the hydrogen atom might occur under suitable conditions. The experiments of Aston, which show that the masses of all atoms except hydrogen are whole numbers, indicate that the close binding of electrons and positive nuclei causes a decrease of mass, owing to the interaction of the fields. Such a decrease of mass might be expected to occur if the supposed close combination of a single hydrogen nucleus and an electron took place. We should expect this decrease of mass to be accompanied by an evolution of energy, since a mass m has energy $\frac{1}{2} mc^2$ associated with it, c being the velocity of light."

The hydrogen discharge tube, 19 cm. long and 2.5 cm. in diameter, was placed in oil, the calorimetric liquid, contained in a Dewar flask. When the discharge traversed the tube the temperature of the oil rose. This was measured by four thermo-junctions in the liquid. Immersed in the same oil was a heating coil. Through this current was passed until the same elevation of oil temperature was attained as had been produced by the operation of the hydrogen tube. Then the two quantities of electrical energy which had caused the same rise of temperature were compared. These agreed to about .3 per cent. for a series of experiments. This shows that "the conservation of energy holds in the energy changes in a discharge tube."

An interesting by-product of calculations in this paper is this, that after an electron has fallen through one volt its energy of translation is equal to that of a gas molecule at 7730° abs. Under the operating conditions of the tube an electron fell through as much as 330 volts. This would correspond to a temperature of 2,600,000° abs. This is of the same order of magnitude as the temperature held by Eddington to obtain in certain types of stars. "In order to account for the fact that the energy radiated by giant stars is too great to be supplied by the loss of gravitational potential energy by contraction, it has been suggested that atomic changes of this nature occur in these stars. If 1 per cent. of the mass of a giant star were converted from hydrogen to helium the energy evolved would be sufficient to supply the star with energy for 1.5×10^7 years." Two hundred ergs per second would be radiated by the mass of the star. Applying this rate to the very small mass of hydrogen in the experimental tube it was found that any effect that might be expected from this radiation was too small to be detected. The hypothesis advanced by Eddington as to the origin of stellar radiation is therefore not affected by the results of this experiment. G. F. S.

THE TRANSFORMATION OF COLOR MIXTURE EQUATIONS FROM ONE SYSTEM TO ANOTHER. II. GRAPHICAL AIDS.*

BY

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INTRODUCTION.

In a previous paper under this title [1] I have outlined the processes necessary for transforming color measurements from one trichromatic system to another, and from a trichromatic to the monochromatic system (spectral hue, luminosity and purity). In the present paper the same problems are considered, but the solutions are worked out in graphical instead of algebraic form. This form of treatment is made possible by consenting, at least during part of the work, to a limitation in the generality of the problems to be handled. This limitation is that the absolute luminosity, or the level in the space figure representing the color system, is not considered. We shall be here concerned primarily when dealing with the two systems of color measurement with the *relative* amounts of our trichromatic primaries and with the *relative* amounts (on a luminosity scale) of spectral color and white.

This limitation of the problems is one which is ordinarily tacitly made in the color measurement of illuminants, for which in fact the principal calculations of the present paper were originally made. With illuminants the luminous values (*e.g.*, candle powers) may be anywhere on a scale of theoretically infinite length, not interrelated in any way with the chromatic character of the light. Luminous values of light sources are customarily the subject of separate determination, and the color measurement normally consists merely of those relative amounts of primaries or of spectral color and white to which we are here initially to be restricted. This case is to be distinguished from that of the color measurement of a transmitting or reflecting medium in which it is usual to measure the luminosity as a fraction, definitely restricted to values between zero (black) and unity (white or complete

* Communicated by the Author.

[1] Jour. Frank. Inst., Dec., 1915, p. 673.

transmission) whatever the value of the illumination, which latter conditions the absolute luminosity.

As the sequel shows, the limitation assumed does not narrow the range of problems amenable to graphical methods as much as the preceding paragraph would suggest. For, by the utilization of data which are accumulated in the complete processes involved, it is possible to solve certain problems in which luminosity values are an essential part. This is notably the case in the measurement of transmitting or reflecting media, for which the graphical methods become in fact very time-saving mechanical aids to performing the calculations outlined in the earlier paper.

The theory of the operations performed in the present paper is all set forth either explicitly, or implicitly, by the treatment of closely similar problems, in the previous paper. Consequently it is considered permissible here to present several specific problems practically as *worked examples*, with a minimum of explanation.

DATA REQUIRED FOR THE SOLUTION OF THE PROBLEMS.

The experimental data necessary to the complete quantitative solution of the problems to be considered are as follows:

1. The amounts of a reference or standard set of trichromatic primaries which must be mixed to reproduce a spectrum of known energy distribution; the plot of these through the spectrum will be referred to as "spectral mixture curves."

2. The distribution of luminosity through a spectrum of known energy distribution.

3. The distribution of energy through the spectrum corresponding to white light.

4. The distribution of energy through the spectrum of the trichromatic primaries which are to be used in making the measurements. These primaries will be referred to as the "working primaries."

For the first of these we shall use the Koenig "fundamental sensation" curves, modified in the manner dictated by consideration of the luminous values of the sensations, as developed in the previous paper. These are shown in Fig. 1 (light lines, arbitrary scale) plotted for an equal energy spectrum, on the basis of equal areas of the red, green and blue curves for a "white light" defined as black body radiation corresponding to 5000° absolute. In Fig. 2 they are shown as plotted for white light so defined, Tables I and II give the numerical values used.

For the distribution of luminosity we shall use the equal energy spectrum luminosity curve or luminous efficiency curve obtained by the present writer and published as an element of "The Photometric Scale."[2] It is also shown in Fig. 1 (heavy line, maximum value unity) and Table I, column 2. This differs slightly from the curve used in the earlier paper.

For the distribution of energy in white light we shall use, as in the earlier paper, the emission curve of a black body at 5000°

TABLE I.

TABLE II.

Equal Energy Spectrum.					White Light Spectrum.				
λ	A	*RS*	*GS*	*BS*	$5000°\ BB$	$A \times BB \frac{L}{5000°}$	*RS*	*GS*	*BS*
.38μ		0.0		0.0	.610		0.0		0.0
.39		.0045		.0757	.641		.0029		.0485
.40	.0024	.0107		.186	.684	.0016	.0073		.127
.41	.0032	.0163		.319	.722	.0023	.0118		.230
.42	.0096	.0190		.482	.758	.0073	.0144		.365
.43	.018	.0148	0.0	.743	.791	.0142	.0117	0.0	.588
.44	.029	.0079	.0048	.929	.821	.0238	.0065	.0039	.763
.45	.041	0.0	.0174	.949	.846	.0347	0.0	.0147	.803
.46	.058	.0010	.0380	.867	.872	.0506	.0009	.0319	.756
.47	.090	.0101	.0670	.705	.893	.0804	.0090	.0598	.630
.48	.138	.0222	.109	.461	.914	.126	.0203	.100	.421
.49	.215	.0617	.165	.233	.932	.200	.0575	.154	.217
.50	.341	.123	.244	.123	.948	.323	.117	.231	.117
.51	.493	.199	.346	.0807	.964	.475	.192	.334	.0778
.52	.638	.275	.453	.0534	.976	.623	.268	.442	.0521
.53	.795	.340	.525	.0366	.986	.784	.335	.518	.0361
.54	.919	.399	.569	.0285	.991	.911	.396	.564	.0282
.55	.992	.441	.577	.0216	.998	.990	.440	.576	.0216
.56	.999	.466	.554	.0167	1.001	1.00	.466	.555	.0168
.57	.953	.470	.494	.0137	1.004	.957	.472	.496	.0138
.58	.879	.462	.394	.0105	1.004	.883	.464	.396	.0105
.59	.777	.438	.287	.0051	1.004	.780	.440	.288	.0051
.60	.633	.398	.198	.0024	1.003	.635	.399	.199	.0024
.61	.491	.348	.133	.0009	1.002	.492	.349	.133	.0009
.62	.362	.289	.0923	.0005	.997	.361	.288	.0921	.0005
.63	.240	.214	.0555	.0002	.992	.238	.212	.0551	.0002
.64	.164	.153	.0340	0.0	.983	.161	.150	.0334	0.0
.65	.101	.0957	.0184		.976	.0986	.0934	.0180	
.66	.060	.0580	.0100		.967	.058	.0561	.0097	
.67	.038	.0344	.0054		.959	.0364	.0380	.0052	
.68	.022	.0148	.0023		.949	.0209	.0140	.0022	
.69	.013	.0096	.0014		.939	.0122	.0090	.0013	
.70	.007	.0052	.0007		.928	.0077	.0048	.0007	

absolute. This is computed from the Wien-Planck equation using the value 14,350 for the constant c_2, and is also shown in Fig. 1, plotted to an arbitrary scale of ordinates;[3] the numerical values are in Table II, column 1. The luminosity curve of the white light spectrum is the product of the luminous efficiency curve by the energy distribution as shown in Table II, column 2.

[2] JOUR. FRANK. INST., August, 1919, p. 217.

[3] This value of c_2 was used because the calibration of a "color temperature" standard lamp from the Bureau of Standards used in the work for which these methods were developed, was on this basis.

For the energy distribution of the working primaries we shall take the transmissions of three special colored glasses, a yellow, a green and a blue, as used in conjunction with a black body at a temperature of 2848° absolute. These primaries are used here because their characteristics have been measured in connection with another problem and are available. Any other set of three colors, well separated in the spectrum, would do as well for our present purpose. The energy distributions of these working primaries are shown in Fig. 3, the ordinates being on an entirely arbitrary scale.

PROBLEM I. TRANSFORMATION OF WORKING PRIMARY MIXING QUANTITIES TO REFERENCE PRIMARY MIXING QUANTITIES.

The first step is to find the reference primary values of the working primaries. This is done by integrating the products $E_\lambda, S_\lambda, d\lambda$ for all three working primaries, where E_λ is the energy value for a given working primary, S_λ the mixing amount of the reference primary for the reference equal energy spectrum at the wave-length λ. This is done graphically, taking the products of the curves of Fig. 3 and Fig. 1, and obtaining the areas of the resultant curves by means of a planimeter. The results of this operation on our chosen primaries are listed in the table below. (The units are of course entirely arbitrary.) For purposes of economy of words the reference primaries will hereafter be spoken of as "sensations," it being understood that the term is correctly applied only to the fundamental primaries which are here used.

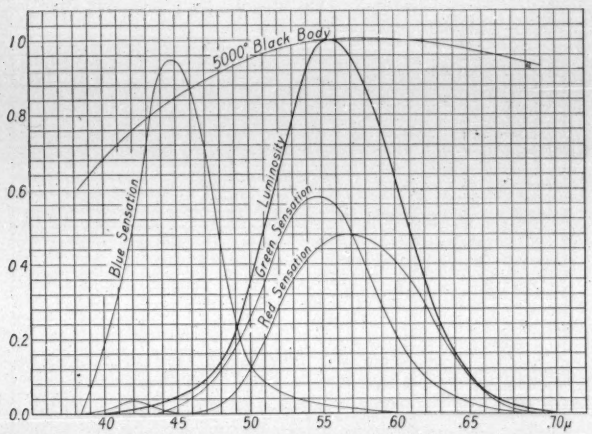
TABLE III.

Working Primary.	Red Sensation.	Green Sensation.	Blue Sensation.
Yellow	.543	.352	.0114
Green	.372	.574	.418
Blue	.426	.494	.979

The sensation values are the coördinates of the working primaries in the rectangular coördinate system in which the three sensations are plotted along the axes, the scale being that for which white light is given by equal quantities of the three sensations. In Fig. 4 the triangle of which the working primaries (Y_1, G_1, B_1) are the vertices is shown in this rectangular coördinate system. We shall call it the "working primary triangle." The straight lines joining these working primary points with the origin of coördinates, and extended, constitute loci of the same

relative proportions of the sensations, or lines of the same hue.[4] These may be produced to cut the plane in which lie all the points for which the sum of the sensation values is unity, on which plane the three coördinate planes mark out the fundamental reference color triangle. We shall call this the "unit-sensation-sum triangle." In order to find where the working primary hues lie in this triangle, it is only necessary to multiply the figures in

FIG. 1.



Fundamental data required for solution of the problems considered: Heavy line; luminosity curve of equal energy spectrum. Lower set of three curves; the fundamental sensations in an equal energy spectrum. Upper curve; energy distribution through the visible spectrum of a black body at 5000° abs. here used as the standard white light.

Table I by such values as shall make the sensation sums unity for each working primary. The figures obtained are as follows:

TABLE IV.

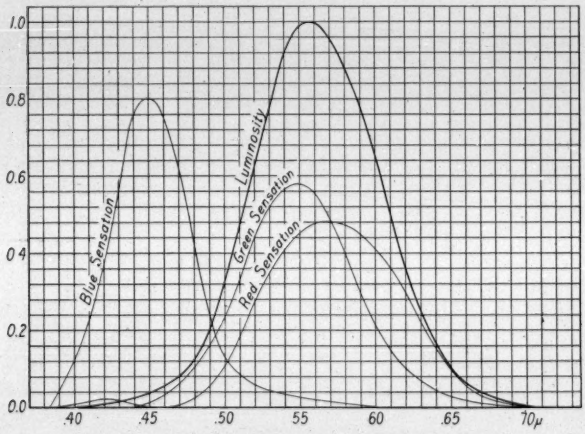
Working Primaries.	Red Sensation.	Green Sensation.	Blue Sensation.
Yellow	.599	.3884	.0126
Green	.273	.421	.306
Blue	.225	.260	.515

[4] The term "hue" is used in conformity with the practice followed in the first paper. The practice of the majority of color terminologists indicates that the term "chroma" would be preferable to designate the straight lines in question, using the term "hue" to designate the planes through these lines and the white-black line.

These sensation values are the coördinates of the vertices of a triangle lying on the unit-sensation-sum triangle, as shown diagrammatically in Fig. 4 (Y_2, G_2, B_2). We shall call this the "working primary hue triangle."

Our problem is now to establish a one-to-one correspondence between points in the working primary triangle and the working primary hue triangle. This is a simple problem in projective geometry. If we call the coördinates of the yellow working primary x_1, y_1, z_1, and that of the blue working primary, x_2, y_2, z_2,

FIG. 2.



Data shown in Fig. 1 as applied to white light (5000° black body).

etc., the sides of the triangle whose vertices are the origin of coördinates and these two working primaries, are of lengths,

$$\text{origin to } Y_1 = \sqrt{x_1^2 + y_1^2 + z_1^2}$$

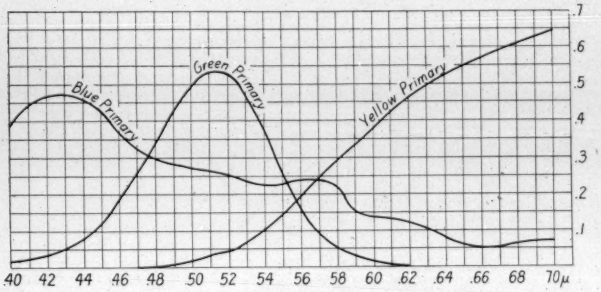
$$\text{origin to } G_1 = \sqrt{x_2^2 + y_2^2 + z_2^2}$$

$$Y_1 \text{ to } G_1 = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

Similarly we can get the three sides of the triangle whose vertices are the origin of coördinates, the yellow and the blue vertices of the working primary hue triangle. These two triangles are shown in Fig. 5. Now we shall assume (as the only reasonable scale to work with) that the sides of the working primary triangle are

divided into equal parts. Dividing the $Y_1 - B_1$ side of the working primary triangle, as shown in Fig. 5, into equal parts, we obtain at once the corresponding divisions on the working primary hue triangle by producing straight lines from the origin through the dividing points as shown. Upon performing the same operation for the other two sides and joining the corresponding points in the three sides we finally obtain the triangle shown in Fig. 6;

FIG. 3.



Spectral energy distribution curves of the three working primaries.

with sides unequally divided, but lying in the fundamental reference plane—the working primary hue triangle.

This triangle is the solution of our first problem. Its manner of use is simple. Suppose a color is measured in terms of the working primaries as of value

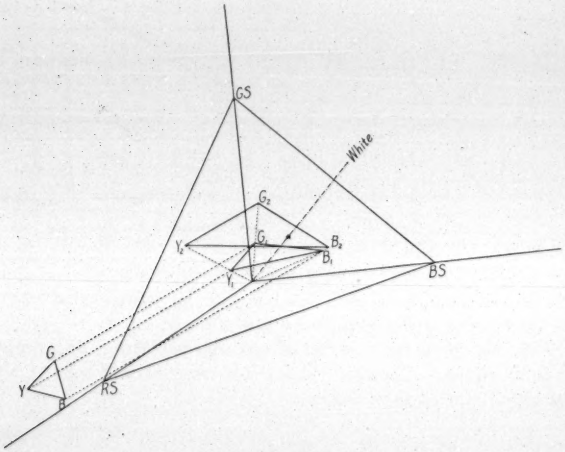
$$Y = y$$
$$G = g$$
$$B = b$$

where $y + g + b = 1$ (either as measured or by reduction). It is now only necessary to lay off a distance y units from the $G - B$ side toward Y, g units from the $Y - B$ side toward G, and b units from the $Y - G$ side toward B, in the small triangle of Fig. 6, to locate a point. The position of this point in the unit-sensation-sum triangle (on a portion of which the working primary hue triangle is superposed) gives the value of the color (or properly its hue) at once in the fundamental units. The procedure is of course reversible, the value of any color given in terms of fundamental sensation units may be transformed to working primary values. Thus the (white) centre of the fundamental triangle,

marked in Fig. 6 by a circle, is immediately read off in terms of our working primaries as $Y = .39$, $G = .25$, $B = .36$.

It may be remarked that a picture is obtained of the various projection processes involved in the transformations outlined by noting that the working primary triangle, with its sides of unequal length but each marked off in equal divisions, is the projection of an equilateral triangle of equally divided sides made by *parallel* rays on a plane at an angle to the plane of the triangle (ortho-

FIG. 4.



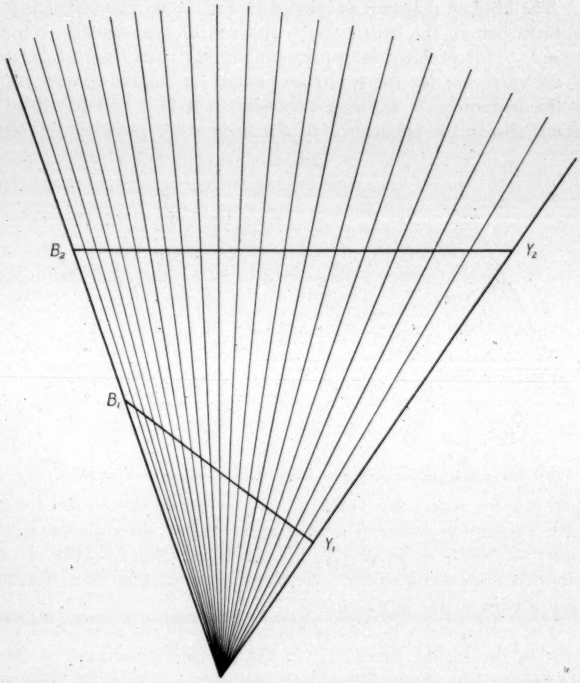
Diagrammatic representation of projection processes for transforming working primary values to fundamental sensation values.

graphic projection); and that the final triangle in the unit-sensation-sum plane is the projection of the working primary triangle on that plane made by divergent rays from the origin of coördinates (stereographic projection). These projection processes are shown diagrammatically in Fig. 4.

At this point it is well to call attention once more to the limitations of the solution we have obtained. It tells us merely the location of the *hue*, that is the *relative* proportions of the three sensation primaries in the color originally measured in terms of the working primaries. This as previously noted is a limitation inherent in the graphical method. It is, however, all the infor-

mation we ordinarily need when measuring illuminants. Where absolute values in the sensation space figure are wanted, they can be arrived at by algebraic methods, provided the coördinates of some common point are known in the two trichromatic systems. In the earlier paper the common point chosen was a reference

FIG. 5.



Process for finding the scale in the unit-sensation-sum plane corresponding to equal divisions in the working primary plane.

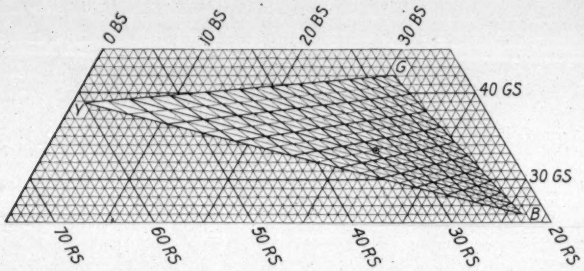
white, and the scales used were such that both sets of measurements evaluated this white as equal admixtures of the three primaries. The same algebraic method is applicable to the present more general problem in which are handled the energy distributions of the primaries as used, irrespective of the color corre-

sponding to any particular scale reading. The algebraic methods necessary for this case as given in the earlier paper are adequate and probably simpler than any graphical solution, since the latter would involve three dimensions.

PROBLEM II. DERIVATION OF MIXTURE CURVES OF THE SPECTRUM.

The kind of diagram developed in Fig. 6 may be utilized in a problem met in the construction and use of trichromatic colorimeters. This problem is the determination of the *mixture curves of the spectrum* for the spectrum patches or colored glasses used as the instrument's working primaries. It is a problem which occurs also in the application of the three-color principle to color

FIG. 6.



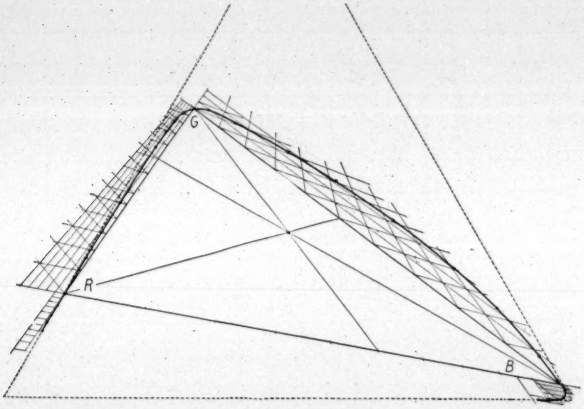
The working primary triangle transferred to the equal-sensation-sum plane.

photography, where the "taking" screen transmissions must conform (assuming uniform photographic action through the spectrum) as closely as possible to the spectral mixture curves of the colors corresponding to the "viewing" screens, thus necessitating a knowledge of the latter curves.

The initial steps in this problem are identical with those set forth in the earlier paper and in the preceding sections of this. We first find by determining their sensation values what amounts of the instrument's primary colors mix to give white; the energy distributions of these primaries in the proportions used constitute the "working primaries." Their relative mixing proportions to yield all the colors in the sensation triangle are determined by constructing a diagram similar to Fig. 6. (Where a large range of colors is to be measured or reproduced the instrument primary

triangle will be relatively much larger and lie closer to the spectrum than does the inner triangle of this figure.) From this the *percentage mixture curves* of the spectrum may be read off at once, that is, the relative amounts of the three primaries, on a scale of maximum value unity, necessary to match the spectral hue at each wave-length. This is as far as the graphical method takes us. The next step is to obtain from these percentage curves the ordinary spectral mixture curves. In these latter the three elements are of the *shapes* which add to give the luminosity curve

FIG. 7.



Projection of Maxwell primary working primary triangle on the modified Koenig sensation triangle.

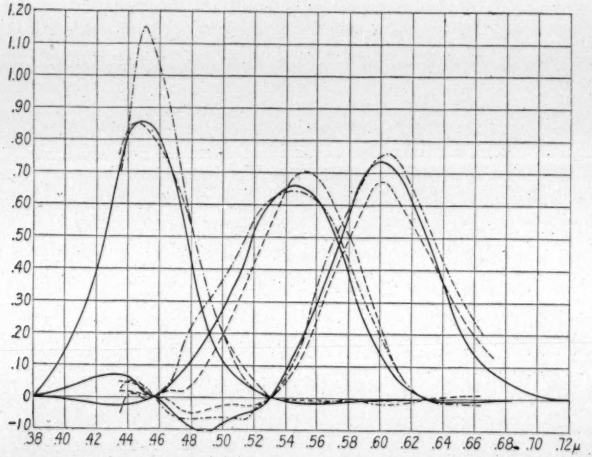
of the spectrum, when the amount of each primary is represented in its luminosity value, but of the *size* dictated by the convention that the areas under the three elementary curves shall be equal for white light.

In order to solve this step of the problem one method would be to utilize the luminosity curve of the (white light) spectrum, and the luminous values of the primaries, as determined from their spectral composition and the equal energy spectrum luminosity curve (Fig. 1). Then, having found, as above, the relative proportions of the three primaries needed to match any wave-length (percentage mixture curves), the rest of the problem is

the purely arithmetical one of finding the actual amounts of the three primaries, taken in these proportions, whose total luminosity shall equal that of the spectrum at the wave-length in question. These actual amounts (on a scale which is determined by the arbitrary choice of spectral patch width and other units in carrying through the work) form, when plotted, the desired mixture curve of the spectrum for the primaries chosen.

The method just outlined depends for its success on a knowl-

FIG. 8.



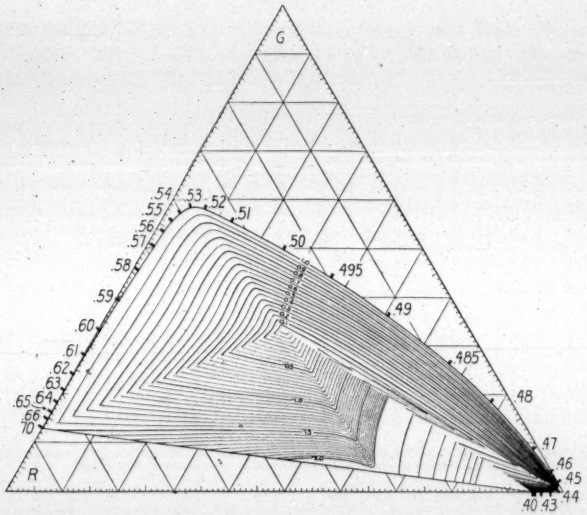
Spectrum mixture curves for Maxwell's primaries, as computed from modified Koenig data (full line). Maxwell's own data are shown by the dashed line, those of his assistant by the dot and dashed line.

edge of the luminous values of the primaries and on the exact agreement of the three-color mixture data with the spectral luminosity curve, *i.e.*, they should be determined by the same observers and under the same conditions. An alternative means is available when the spectrum mixture curves of the fundamental primaries (*e.g.*, sensations) are known, as has been assumed. This method consists in taking at each wave-length such quantities of the working primaries in the proportions indicated by the percentage mixture curves as shall together give the amounts of the fundamental primaries present, as shown on the mixture curves of the latter.

In practice it is only necessary to assure that one of the fundamental primaries is present in proper quantity, for instance, the red through the orange and red, the green through the yellow and green, etc.

Using this latter method I have determined, as a matter of interest, the mixing proportions of the three primaries used by Maxwell in his pioneer investigation in 1859. Fig. 7 shows the

FIG. 9.



The fundamental sensation triangle, showing (outer curve) the position of the spectrum, (inner curves) the amounts of the spectral colors, on a luminosity scale, to be mixed with white to match all colors from white to spectrum.

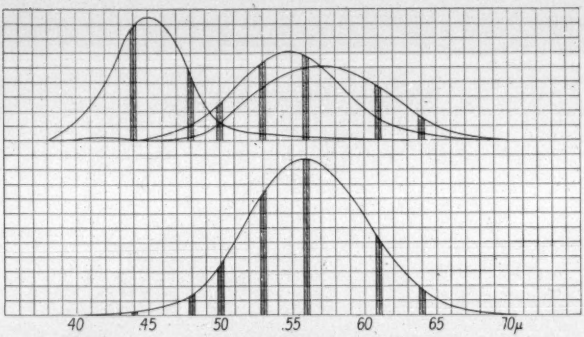
necessary parts of the working primary triangle as projected on the sensation triangle, where the wave-length scale on the spectrum is as in Fig. 9, and Fig. 8 shows the spectrum mixture curves as computed therefrom (full lines). The dashed and dot and dashed lines are the data of Maxwell's two observers as reduced to a normal spectrum. The agreement thus shown between Maxwell's observers and the mean observer represented by Koenig's curves, as arranged and transformed in the first paper of this study, is on the whole surprisingly good.

Attention may here be called to the fact that statistical studies of color vision, such as are desirable to establish an average eye for purposes of color specification, could be most simply made by determining mixture curves of the spectrum with some convenient set of three primaries, as done by Maxwell. These curves could then be transformed to any set of primaries decided upon as rational, by the transformation methods here set forth.

PROBLEM III. TRANSFORMATION FROM TRICHROMATIC TO MONOCHROMATIC SYSTEM.

We shall take as our trichromatic system the fundamental sensation system defined by the curves of Fig. 1. Any other tri-

FIG. 10.



Luminosity curve and sensation curves for white light (5000° black body), divided into strips for transformation process from trichromatic to monochromatic system.

chromatic system defined by a set of spectrum mixture curves could be used equally well. The spectrum in the fundamental sensation system is represented in the unit-sensation-sum triangle by the curve, marked in wave-lengths, of Fig. 9.

The first step is to plot to the same wave-length scale both the luminosity distribution, and the sensation distribution for white light, the data for which occur in Table II, columns 2, 3, 4 and 5, and in Fig. 2. The resultant curves are shown in Fig. 10 (arbitrary scales). Next we divide the spectrum into a large number of narrow strips of equal width, of which several are shown in the figure, the width being small enough so that each is substantially monochromatic. In the present case the strip width chosen was

.004μ. The third step is to find the sensation values of each strip, in terms of the sensation values for the integral spectrum, that is, the area in the strip under each of the three sensation curves, referred to the total area under the corresponding curve taken as 1/3. To illustrate, in the strip .478μ to .482μ the sensation curve areas included are, in terms of the sum of the total white light sensation as unity,

$$RS = .00059 \quad GS = .0026 \quad BS = .0106$$

In the rectangular coördinate system in which white light corresponds to equal sensations, these spectral strips form a series of points lying along a closed curve very close to the origin of coördinates (C_1, Fig. 11).

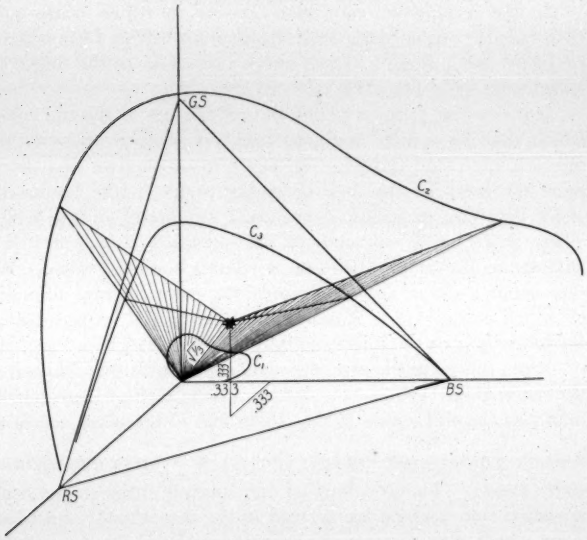
It is now our purpose to find the coördinates of spectral colors which shall be *equally luminous with the integral white* of the unit-sensation-sum triangle. In order to do this we first determine the areas of the monochromatic strips in the luminosity curve diagram, in terms of the total luminosity of the white. These determined, we multiply the sensation coördinates just obtained by the reciprocals of these relative luminous values. We thus obtain a second spectral curve in the space diagram all points of which correspond to equally luminous spectral strips, each of the luminosity of the integral white (C_2, Fig. 11).

From this point the procedure is identical with that outlined in the last section. We find the distances from each of these equally luminous spectral points to the origin and to the white centre of the unit-sensation-sum triangle (distant $\sqrt{\frac{1}{3}}$ from the origin of coördinates). The positions of the spectral strips in the unit-sensation-sum triangle are derived in the way already described, from which their distances to the origin of coördinates and the white centre are fixed. These positions form a curve which is the one shown in Fig. 9, marked with wave-lengths. We then have for each strip two triangles with the same vertex and vertex angle, the base of one of which lies in the unit-sensation-sum plane, while the base of the other connects the white point in that plane with the equally luminous spectral color. This latter base line we divide into equal parts, and join the dividing points to the origin by straight lines. The points where these lines cut the plane of the unit-sensation-sum triangle are the dividing-points on the

line in that plane connecting the white point with the hue of the spectral strip, corresponding to our equally spaced scale between equally luminous white and spectral color. The whole process is shown diagrammatically in Fig. 11.

It is now only necessary to perform this operation for a sufficient number of wave-lengths to cover the spectrum, after which the resultant points are to be joined up into curves as shown in

FIG. 11.



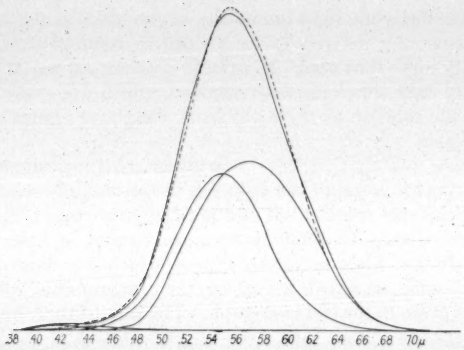
Diagrammatic representation of the projection processes for transforming sensation values to spectral hue and relative amounts of spectral color and white.

Fig. 9. In this figure any color (hue) is represented by a point; its spectral hue is obtained by producing the line joining the point and the white centre until it cuts the spectrum curve. The amount of spectral color on a luminous scale necessary to take to match the color (purity or saturation) is the length of this same line measured from the white centre and read off from the intercepting curves, which are numbered from zero (white centre) to 1.00 (spectral color). The amount of white is the difference between

this number and 1.00. For instance, 1.00 $C = .15\lambda + .85\ W$. For purples the scales have simply been continued to negative values. The equation of a purple is formed in the same way as for any other color, that is, so that the sum of spectral color and white shall be 1.00. For instance, 1.00 $C = -.15\lambda + 1.15\ W$, or 1.00 $C + .15\lambda = 1.15\ W$.

The background of the diagram, Fig. 9, is the fundamental sensation triangle; points on either system can be located on the other by the use of a straight edge. A convenient way to print

FIG. 12.



The three sensation curves for white light plotted according to their luminous values. Their sum is the upper full line curve; the dashed line is the luminosity curve for white light.

diagrams of this sort would be to have each set of coördinates in a different color, so that they could overlap without confusion.

Thus far the process developed is adequate only for fixing the hue of a color, that is, we have merely its spectral hue and purity in the monochromatic system, or its relative proportions of red, green and blue, on the trichromatic system. These, as earlier noted, are all of the data ordinarily required in the color measurement of illuminants. In order to make the complete transformation of measurements from one system to the other, we must know the luminosity values of the trichromatic primaries; in this case of the three fundamental sensations. We have thus far in the present treatment steered clear of assigning luminosity values to the sensations, although each monochromatic strip used in the

processes based on Fig. 10 actually gives values for one of a set of simultaneous equations from which these may be obtained. In the earlier paper luminous values for the fundamental sensations were derived by the solution of such equations. In order to fit the luminosity curve of the equal energy spectrum used in the present paper slightly different values are necessary, as follows:

Luminous value of red sensation in white light	.568
Luminous value of green sensation in white light	.426
Luminous value of blue sensation in white light	.006

It may be noted that the summation of the three sensation curves with their weights assigned as shown in Fig. 12 gives a check with the white light luminosity curve which is not as close as the previously derived values yielded in connection with the luminosity curve then used. In default, however, of sensation and luminosity data simultaneously obtained, which are really necessary for the solution of these problems, the above figures are the best available.[5]

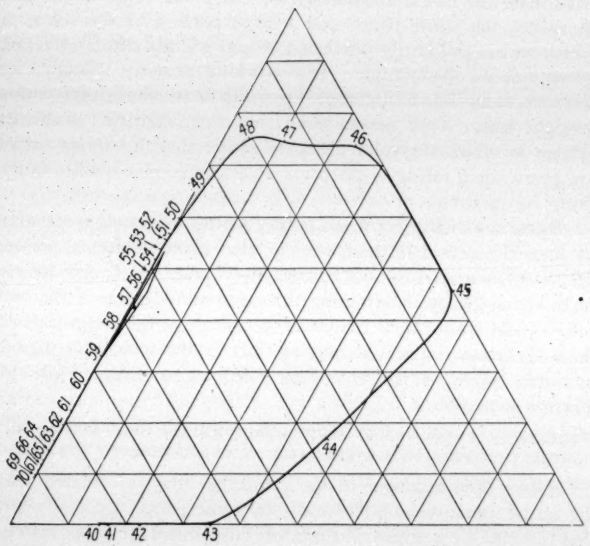
Suppose now that we have a complete color measurement on the trichromatic system. To reduce it to the monochromatic system we derive its spectral hue and purity by the use of Fig. 9 as already described. To obtain its luminosity value, we have merely to multiply the three sensation values, which are expressed in terms of some standard white, by their appropriate luminous values, as given in the last paragraph. The sum of these luminous

[5] F. Exner has recently (*Wien. Ber.*, 1921, p. 27) made a determination of the relative luminous values of the three Koenig sensation curves by an equivalent though less direct method than that used by the writer. His values are, on the unit-sum scale here used, $R = .562$, $G = .425$, $B = .013$. Exner notes the fact pointed out in the writer's 1915 paper, that no possible value can be assigned to Koenig's red curve which will permit the luminously evaluated sum to match the white light luminosity curve. Exner remedies this by arbitrarily amputating the second elevation of the red curve in the blue region of the spectrum, considering the original observations as sufficiently ill determined to warrant this. He then so modifies the remaining curves that the crossing points of the three are still in agreement with his own earlier determination. The position of the crossing points is altered by the shift in the blue primary which was the means selected by the writer to modify the Koenig curves while not conflicting with Koenig's observed values. These crossing points differ so considerably with different observers, as is shown by spectral hue discrimination data, as to make them fully as uncertain as Koenig's data. This whole matter of the exact correlation of color mixture and luminosity data offers a large field for research.

values is the desired third factor, namely, the luminosity of the color.

Conversely, if we have a complete color measurement on the monochromatic system, we obtain its relative red, green and blue proportions by the use of Fig. 9. The absolute red, green and blue sensation values are obtained by first multiplying the relative

FIG. 13.



Color triangle in the coördinate system whose units are equal luminous values of the sensations.

sensation values by their respective luminosities, and then finding the constant by which the sum of their luminosities must be multiplied to make it equal to the measured total luminosity. This constant is the figure by which the three relative sensation values must be multiplied to yield absolute sensation values.

In connection with the use of the luminous values of the reference primaries, it may well be asked why recourse is not made at once to the color mixture coördinate system in which the units are *equal luminous values* of the primaries. In such a system, points

in the color triangle (unit-sensation-sum plane) would be all of equal luminous value, and the problem of determining amounts of spectrum color and white would be one of direct measurement on a scale of equal divisions. In order to illustrate this possibility with its practical disadvantages, I have, in Fig. 13, plotted the spectrum in the color triangle form from the sensation curves as given in their luminous values in Fig. 12. It will be obvious at once that, due to the excessively low luminous value of the blue sensation, the white point, and a large portion of the colors in which we are ordinarily interested lie unworkably close to the red-green side of the triangle. Our working primary triangle, for instance, is as shown, flattened down almost to coincidence with a straight line. This makes clear that the ordinary coördinate system in which the color elements rather than luminous values are given equal rating is far preferable where color quality is the thing in question.

By means of Fig. 13 it is a simple matter to answer a question of some theoretical interest, namely, the *relative luminous values of complementaries in the spectrum.* These are found simply in this triangle by determining the relative distances of the two colors from white; their luminous values are as the reciprocals of these distances. The outstanding fact is the almost negligible luminous value of the blue light adequate to make white by mixture with yellow.

PROBLEM IV. REDUCTION OF SPECTROPHOTOMETRIC TRANSMISSION OR REFLECTION DATA TO TRICHROMATIC OR MONOCHROMATIC SYSTEMS.

It has been assumed in the problems thus far treated that the actual measurements are made on some form of colorimeter, that is, either by a three-color mixture instrument, or by an instrument measuring luminosity, spectral hue, and purity. An interesting case from the standpoint of *color specification* is offered where the actual measurements made are those of reflection or transmission at each wave-length, by a spectrophotometer, which are then reduced to trichromatic or monochromatic values, for simplicity of description. The advantage, other than simplicity, offered by this scheme is that the spectrophotometric values are not subject to variations due to the color vision of the observer, as are true color measurements; the original spectrophotometric data provide the full information necessary for the manufactory or standard-

izing laboratory, while the derived color sensation or hue, luminosity, and purity values provide all the information in which the user of such a commodity as a paper or paint is ordinarily interested.

The reduction of spectrophotometric reflection or transmission data to either of the color systems is performed by fairly obvious applications of the data given, and may be most easily presented in the form of *instructions.* Ordinarily the color values desired are for white light, consequently we use the data of columns 2, 3, 4 and 5, Table I, and Fig. 2.

I. *Reduction to Color Sensations.*—Multiply the transmission or reflection factor at each wave-length by the red, green and blue sensation values (Fig. 2). The areas of the resultant curves, expressed as fractions of the areas of the original curves, are the required sensation values.

II. *Reduction to Spectral Hue, Luminosity and Purity.*—Multiply the transmission or reflection factor at each wave-length by the white light spectral luminosity curve (Fig. 2). The area of the resultant curve, expressed as a fraction of the original luminosity curves gives the *luminosity, i.e.,* the integral visual reflection or transmission factor.

(An alternative method is to give to each sensation value, as derived under I, its luminous value. Thus if the red sensation value is multiplied by .568, the green by .426, and the blue by .006, the sum of these figures is the luminosity. Since, however, the luminosity curve is better determined than the luminous values of the sensations the method of the preceding paragraph is preferable, although it involves an extra operation.)

Next obtain the sensation values as above, multiply them by such a factor as to make their sum after multiplication, *unity.* On the unit-sensation-sum triangle (Fig. 9) locate the hue by finding the point where the red, green and blue coördinates (vertical distances from each side toward the corner corresponding to the primaries) are the three unit-sum sensations just obtained. To find the *spectral hue,* draw a line from the centre of the triangle (white) through the point, continuing it to cut the spectrum, and read off the wave-length. The *purity* (amount of spectral color in luminous units) is read off the intersected curves which are roughly concentric with the white point.

Illustrations.—An orange of medium saturation could have values

Luminosity	.43
Spectral hue	.601μ
Purity	.74

A purple would be represented by its complementary hue, and its purity by a minus value, thus:

Luminosity	.34
Spectral hue	(.50μ)
Purity	−.22

DISCUSSION.

It need hardly be pointed out that while in each of the problems considered the numerical results are dependent on the particular trichromatic reference frames chosen, the results obtained for the reductions to hue, luminosity and purity will check with direct experiment only if the spectral mixture and luminosity curves used are consistent with each other. In the case here considered this means the consistency of the modified Koenig sensation curves with the spectral luminous efficiency curves used. It is hardly likely that the meagre data of the Koenig curves will be sufficiently in agreement with the much better determined spectral luminous efficiency curve to guarantee a close experimental check. Color measurements of illuminants made both by trichromatic and monochromatic methods, against the same standard white, would show how closely these reference curves agree, but exact data of this sort are at present lacking. The methods developed in the paper are, however, general, and applicable to more complete experimental data when available. The status of the whole problem of color measurement and specification would be materially advanced by the determination of a set of trichromatic mixture curves of the spectrum, using some well-considered set of primaries (which need not necessarily be the fundamental sensations) these curves to correspond to the same average eye and conditions of observation as does the comparatively well-determined spectral luminous efficiency curve.

ELECTRICAL OSCILLATIONS ON LINES.*

BY

LOUIS COHEN, Ph.D.

Consulting Engineer, Signal Corps, U.S.A.

THE subject of electrical oscillations on lines is of continuously growing importance in electrical engineering. It extends to all branches—telephony, telegraphy, power transmission, etc.—and also irrespective of the character of the electromotive force impressed direct or alternating. Whenever a change occurs in the circuit conditions, a transient effect is introduced which generally assumes the character of oscillations or wave propagations on the line. The circuit condition changes which are inevitably present in all systems are those which occur at the instant of closing or opening of the circuit.

A knowledge of what occurs on the system during the establishment of the steady state is of great importance. In the case of telegraphy, for instance, the transient effects produced by the signalling are predominant, and the speed of signalling, particularly in the case of ocean cable telegraphy, is governed and determined by these effects. In power transmission, the transient effects may at times assume a character of destructive proportions, and must be understood and carefully guarded against. The problems presented by these effects are generally complex in their nature and cannot be readily subjected to experimental investigations. Mathematical analysis must be relied upon for the study and understanding of the phenomena associated with these transient effects.

The importance of this subject was fully appreciated by engineers for some time, and many valuable papers covering different phases of the subject can be found in engineering literature. The subject, however, is so large and complex that any new presentation of it which will help to make the subject more intelligible to the engineers, throw additional light on it, and perhaps facilitate the solution of the many problems that may arise in connection with it, should prove of value. It is believed that the method developed in this paper for the solution of this class of

* Communicated by General George O. Squier, Chief Signal Officer, U. S. A., and Associate Editor of this JOURNAL.

problems offers many advantages in the matter of directness and simplicity. A limited number of cases are worked out, but the method is applicable to the solution of many others. The application of the formulæ derived here to some practical problems will be considered in another paper.

Those who are acquainted with Heaviside's publications will recognize that I have made use of the expansion processes developed with such great skill by Doctor Heaviside, and have adopted them for the methods developed in this paper. I am, of course, under deep obligations to Doctor Heaviside's writings for the inspiration and suggestions derived from them.

Consider the case of a line of uniformly distributed inductance, capacity, resistance and leakage, these being designated by L, C, R, and g, respectively. The current voltage relations at any point on the line are expressed by the following equations:

$$\left.\begin{aligned} L\frac{dI}{dt} + RI &= -\frac{dV}{dx}, \\ C\frac{dV}{dt} + gV &= -\frac{dI}{dx}. \end{aligned}\right\} \tag{1}$$

Designate by p the time differential operator $\left(p = \frac{d}{dt}\right)$, and the above take the forms:

$$\left.\begin{aligned} (Lp + R)\, I &= -\frac{dV}{dx}, \\ (Cp + g)\, V &= -\frac{dI}{dx}. \end{aligned}\right\} \tag{2}$$

We may eliminate either I or V from the above equations, from which results the well-known equation of propagation:

$$\frac{d^2V}{dx^2} = q^2V, \tag{3}$$

where

$$q^2 = (Lp + R)\,(Cp + g). \tag{4}$$

The solution of equation (4) is

$$V = Ae^{qx} + Be^{-qx}. \tag{5}$$

By the aid of the first equation of (2) we get the expression for the current:

$$I = \frac{q}{Lp + R}\left\{-Ae^{qx} + Be^{-qx}\right\}. \tag{6}$$

Equations (5) and (6) are the general solutions for the voltage and current, the constants A and B to be determined by the terminal conditions in each special case.

LINE GROUNDED AT ONE END.

Assume a sinusoidal e.m.f. of frequency $\frac{\omega}{2\pi}$, $e = E\varepsilon^{j\omega t}$, impressed at one end of the line, and the other end being grounded, the terminal conditions in this case are:

$$\left.\begin{aligned} x = o,\ V &= E\varepsilon^{j\omega t}, \\ x = l,\ V &= o. \end{aligned}\right\} \tag{7}$$

Substituting in (5), we get

$$\left.\begin{aligned} A + B &= E\varepsilon^{j\omega t}, \\ A\varepsilon^{ql} + B\varepsilon^{-ql} &= o. \end{aligned}\right\} \tag{8}$$

From these two equations the two constants A and B are determined:

$$\left.\begin{aligned} A &= \frac{-E\varepsilon^{-ql}\varepsilon^{j\omega t}}{\varepsilon^{ql} - \varepsilon^{-ql}} \\ B &= \frac{E\varepsilon^{ql}\varepsilon^{j\omega t}}{\varepsilon^{ql} - \varepsilon^{-ql}} \end{aligned}\right\} \tag{9}$$

Substituting in (5) the resulting equation for the potential at any point on the line at distance X is:

$$V = E\frac{\operatorname{Sinh} q\,(l-x)}{\operatorname{Sinh} q\,l}\varepsilon^{j\omega t}. \tag{10}$$

In the above expression q includes the time differential operator which is so far indeterminate. For the steady state in the case of a sinusoidal e.m.f., the problem is very simple; operating by p on $\varepsilon^{j\omega t}$ gives $j\omega\varepsilon^{j\omega t}$. The complete solution, however, to include the transient as well as the steady state, for either an alternating or a direct impressed e.m.f., the problem offers some difficulties. In the following a new method is proposed for the solution of this problem, which is believed to be novel and applicable to many other problems of this class. We may write equation (10) in the following form:

$$V = \frac{\operatorname{Sinh} q\,(l-x)}{q\,l}\ \frac{q\,l}{\operatorname{Sinh} q\,l}\ E\varepsilon^{j\omega t} \tag{11}$$

By trigonometry

$$\frac{q\,l}{\operatorname{Sinh} q\,l} = 1 - 2q^2l^2\left\{\frac{1}{\pi^2 + q^2l^2} - \frac{1}{(2\pi)^2 + q^2l^2} + \frac{1}{(3\pi)^2 + q^2l^2} - \cdots\right\} \tag{12}$$

where

$$q^2l^2 = p^2(Lp+R)\ (Cp+g) = p^2LC\left\{p^2 + p\left(\frac{R}{L} + \frac{g}{C}\right) + \frac{Rg}{LC}\right\}.$$

Put for brevity

$$v^2 = \frac{1}{LC}, \quad \frac{R}{L} = 2a, \quad \frac{g}{C} = 2b, \tag{13}$$

we get

$$q^2 l^2 = \frac{l^2}{v^2} \left\{ p^2 + 2(a+b)p + 4ab \right\} \tag{14}$$

and

$$\frac{1}{\pi^2 + q^2 l^2} = \frac{v^2}{l^2} \frac{1}{p^2 + 2(a+b)p + 4ab + \frac{\pi^2 v^2}{l^2}}. \tag{15}$$

The denominator in equation (15) may be put in the following form:

$$p^2 + 2(a+b)p + 4ab + \frac{\pi^2 v^2}{l^2} = (p - k_1)(p - k_1'), \tag{16}$$

where

$$\left.\begin{aligned} k_1 &= -(a+b) + \sqrt{(a-b)^2 - \frac{\pi^2 v^2}{l^2}}, \\ k_1' &= -(a+b) - \sqrt{(a-b)^2 - \frac{\pi^2 v^2}{l^2}}. \end{aligned}\right\} \tag{17}$$

Hence,

$$\frac{1}{\pi^2 + q^2 l^2} = \frac{v^2}{l^2} \frac{1}{(p - k_1)(p - k_1')}. \tag{18}$$

By partial fractions equation (18) may be put in another form as follows:

$$\frac{1}{\pi^2 + q^2 l^2} = \frac{v^2}{l^2 (k_1 - k_1')} \left\{ \frac{1}{p - k_1} - \frac{1}{p - k_1'} \right\}. \tag{19}$$

The other terms of equation (12) may be put in a form similar to (19) as follows:

$$\left.\begin{aligned} \frac{1}{(2\pi)^2 + q^2 l^2} &= \frac{v^2}{l^2 (k_2 - k_2')} \left\{ \frac{1}{p - k_2} - \frac{1}{p - k_2'} \right\}, \\ \frac{1}{(3\pi)^2 + q^2 l^2} &= \frac{v^2}{l^2 (k_3 - k_3')} \left\{ \frac{1}{p - k_3} - \frac{1}{p - k_3'} \right\}, \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \frac{1}{(n\pi)^2 + q^2 l^2} &= \frac{v^2}{l^2 (k_n - k_n')} \left\{ \frac{1}{p - k_n} - \frac{1}{p - k_n'} \right\}, \end{aligned}\right\} \tag{20}$$

where

$$\left.\begin{aligned} k_2, k_2' &= -(a+b) \pm \sqrt{(a-b)^2 - \left(\frac{2\pi v}{l}\right)^2}, \\ k_3, k_3' &= -(a+b) \pm \sqrt{(a-b)^2 - \left(\frac{3\pi v}{l}\right)^2}, \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ k_n, k_n' &= -(a+b) \pm \sqrt{(a-b)^2 - \left(\frac{n\pi v}{l}\right)^2}. \end{aligned}\right\} \tag{21}$$

Expand each of the terms $\frac{1}{p-k}$ in a series as follows:

$$\frac{1}{p-k_1} = \frac{1}{p}\left(1-\frac{k_1}{p}\right)^{-1} = \frac{1}{p}\left\{1+\frac{k_1}{p}+\frac{k_1^2}{p^2}+\frac{k_1^3}{p^3}+\cdots\right\} \quad (22)$$

Operate by this series an $\varepsilon^{j\omega t}$ which is simply successive time integration, the limits of integration being zero and t. Replace $j\omega$ by γ for brevity and we get

$$\left.\begin{aligned}
&\frac{1}{p}\varepsilon^{\gamma t} = \int_0^t \varepsilon^{\gamma t} = \frac{1}{\gamma}\varepsilon^{\gamma t} - \frac{1}{\gamma}\\
&\frac{1}{p^2}\varepsilon^{\gamma t} = \frac{1}{\gamma^2}\varepsilon^{\gamma t} - \frac{1}{\gamma^2} - \frac{1}{\gamma}t\\
&\frac{1}{p^3}\varepsilon^{\gamma t} = \frac{1}{\gamma^3}\varepsilon^{\gamma t} - \frac{1}{\gamma^3} - \frac{1}{\gamma^2}t - \frac{1}{\gamma}\frac{t^2}{\lfloor 2}\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&\frac{1}{p^n}\varepsilon^{\gamma t} = \frac{1}{\gamma^n}\varepsilon^{\gamma t} - \frac{1}{\gamma^n} - \frac{1}{\gamma^{n-1}}t - \frac{1}{\gamma^{n-2}}\frac{t^2}{\lfloor 2} - \cdots \frac{1}{\gamma}\frac{t^{n-1}}{\lfloor n-1}
\end{aligned}\right\} \quad (23)$$

Assembling all the terms and arranging them in suitable order, we have

$$\left.\begin{aligned}
\frac{1}{p-k_1}\varepsilon^{\gamma t} = \frac{1}{p}\Big\{ &\varepsilon^{\gamma t}\left(1+\frac{k_1}{\gamma}+\frac{k_1^2}{\gamma^2}+\frac{k_1^3}{\gamma^3}+\cdots\right)\\
&-\frac{k_1}{\gamma}\left(1+\frac{k_1}{\gamma}+\frac{k_1^2}{\gamma^2}+\cdots\right)\\
&-\frac{k_1}{\gamma}\,k_1 t\left(1+\frac{k_1}{\gamma}+\frac{k_1^2}{\gamma^2}+\cdots\right)\\
&-\frac{k_1}{\gamma}\,\frac{k_1^2 t^2}{\lfloor 2}\left(1+\frac{k_1}{\gamma}+\frac{k_1^2}{\gamma^2}+\cdots\right)
\end{aligned}\right\} \quad (24)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

The above is equivalent to

$$\frac{1}{p-k_1}\varepsilon^{\gamma t} = \frac{1}{p}\left\{\frac{\varepsilon^{\gamma t}}{1-\frac{k_1}{\gamma}} - \frac{k_1}{\gamma}\frac{\varepsilon^{k_1 t}}{1-\frac{k_1}{\gamma}}\right\}. \quad (25)$$

Similarly

$$\frac{1}{p-k_1'}\varepsilon^{\gamma t} = \frac{1}{p}\left\{\frac{\varepsilon^{\gamma t}}{1-\frac{k_1'}{\gamma}} - \frac{k_1'}{\gamma}\frac{\varepsilon^{k_1' t}}{1-\frac{k_1'}{\gamma}}\right\}. \quad (26)$$

Substituting from (25) and (26) into (19) results the relation

$$\frac{1}{\pi^2+q^2\beta^2}\varepsilon^{\gamma t} = \frac{v^2}{l^2(k_1-k_1')}\frac{1}{p}\left\{\frac{\gamma\varepsilon^{\gamma t}}{\gamma-k_1} - \frac{\gamma\varepsilon^{\gamma t}}{\gamma-k_1'} - \frac{k_1\varepsilon^{k_1 t}}{\gamma-k_1} + \frac{k_1'\varepsilon^{k_1' t}}{\gamma-k_1'}\right\}. \quad (27)$$

Operating on the bracket term of (27) by $\frac{1}{p}$, which is time integration, we get

$$\frac{1}{p}\left\{\frac{\gamma\varepsilon^{\gamma t}}{\gamma-k_1}-\frac{\gamma\varepsilon^{\gamma t}}{\gamma-k_1'}-\frac{k_1\varepsilon^{k_1 t}}{\gamma-k_1}+\frac{k_1'\varepsilon^{k_1' t}}{\gamma-k_1'}\right\}=\left\{\frac{\varepsilon^{\gamma t}}{\gamma-k_1}-\frac{1}{\gamma-k_1}-\frac{\varepsilon^{\gamma t}}{\gamma-k_1'}+\frac{1}{\gamma-k_1'}\right.$$
$$\left.-\frac{\varepsilon^{k_1 t}}{\gamma-k_1}+\frac{1}{\gamma-k_1}+\frac{\varepsilon^{k_1' t}}{\gamma-k_1'}-\frac{1}{\gamma-k_1'}\right\}=\varepsilon^{\gamma t}\left\{\frac{1}{\gamma-k_1}-\frac{1}{\gamma-k_1'}\right\}-\frac{\varepsilon^{k_1 t}}{\gamma-k_1}+\frac{\varepsilon^{k_1' t}}{\gamma-k_1'}. \tag{28}$$

We finally obtain

$$\frac{1}{\pi^2+q^2l^2}\varepsilon^{\gamma t}=\frac{v^2}{l^2(k_1-k_1')}\left\{\varepsilon^{\gamma t}\left(\frac{1}{\gamma-k_1}-\frac{1}{\gamma-k_1'}\right)-\frac{\varepsilon^{k_1 t}}{\gamma-k_1}+\frac{\varepsilon^{k_1' t}}{\gamma-k_1'}\right\}. \tag{29}$$

It is obvious by inspection that the first part of the bracket term of above equation is exactly of the same form as (19) except that p is replaced by γ. We may therefore write above equation in the following form:

$$\frac{1}{\pi^2+q^2l^2}=\frac{1}{\pi^2+s^2l^2}\varepsilon^{\gamma t}+\frac{v^2}{l^2(k_1-k_1')}\left\{\frac{\varepsilon^{k_1' t}}{\gamma-k_1'}-\frac{\varepsilon^{k_1 t}}{\gamma-k_1}\right\}, \tag{30}$$

where

$$s^2=\frac{1}{v^2}\left\{\gamma^2+2\gamma(a+b)+4ab\right\}. \tag{31}$$

Applying the same process to the other terms of equation (12), we shall have:

$$\left.\begin{aligned}
&\frac{1}{(2\pi)^2+q^2l^2}\varepsilon^{\gamma t}=\frac{1}{(2\pi)^2+s^2l^2}\varepsilon^{\gamma t}+\frac{v^2}{l^2(k_2-k_2')}\left\{\frac{\varepsilon^{k_2' t}}{\gamma-k_2'}-\frac{\varepsilon^{k_2 t}}{\gamma-k_2}\right\},\\
&\frac{1}{(3\pi)^2+q^2l^2}\varepsilon^{\gamma t}=\frac{1}{(3\pi)^2+s^2l^2}\varepsilon^{\gamma t}+\frac{v^2}{l^2(k_3-k_3')}\left\{\frac{\varepsilon^{k_3' t}}{\gamma-k_3'}-\frac{\varepsilon^{k_3 t}}{\gamma-k_3}\right\},\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&\frac{1}{(n\pi)^2+q^2l^2}\varepsilon^{\gamma t}=\frac{1}{(n\pi)^2+s^2l^2}\varepsilon^{\gamma t}+\frac{v^2}{l^2(k_n-k_n')}\left\{\frac{\varepsilon^{k_n' t}}{\gamma-k_n'}-\frac{\varepsilon^{k_n t}}{\gamma-k_n}\right\}.
\end{aligned}\right\} \tag{32}$$

It will be shown presently that the terms in equation (32), which contain the factor $\varepsilon^{\gamma t}$, are parts of the expression which gives the steady state of the voltage on the line, and the terms containing the factors $\varepsilon^{k_n t}$, $\varepsilon^{k_n' t}$ represent the transient part of the voltage. We may consider them separately, designating the part contributing only to the steady state by the subscript s, and the other part by the subscript t. Consider first the $\varepsilon^{\gamma t}$ terms, and we have

$$\frac{ql}{\operatorname{Sinh} ql}\varepsilon^{\gamma t}(s)=\left\{1-2q^2l^2\left(\frac{1}{\pi^2+s^2l^2}-\frac{1}{(2\pi)^2+s^2l^2}+\cdots\right)\right\}\varepsilon^{\gamma t} \tag{33}$$

Operating by q^2l^2 on $\varepsilon^{\gamma t}$ involves complete differentiation which in this case would only change the p's to γ's in the q expression and consequently change q^2l^2 to s^2l^2, hence

$$\frac{ql}{\operatorname{Sinh} ql}\varepsilon^{\gamma t} = \left\{1 - 2s^2l^2\left(\frac{1}{\pi^2 + s^2l^2} - \frac{1}{(2\pi)^2 + s^2l^2} + \frac{1}{(3\pi)^2 + s^2l^2} - \cdots\right)\right\}\varepsilon^{\gamma t}$$
$$= \frac{sl}{\operatorname{Sinh} sl}\varepsilon^{\gamma t}. \tag{34}$$

To get the complete solution for the steady voltage, we must now operate on (34) by the factor $\frac{\operatorname{Sinh} q(l-x)}{ql}$, see equation (11). Now

$$\frac{\operatorname{Sinh} q(l-x)}{ql} = \frac{q(l-x) + \frac{q^3(l-x)^3}{\lfloor 3} + \frac{q^5(l-x)^5}{\lfloor 5} + \cdots\cdots}{ql}$$
$$= \left(1 - \frac{x}{l}\right) + \frac{q^2\left(1 - \frac{x}{l}\right)^3}{\lfloor 3} + \frac{q^4\left(1 - \frac{x}{l}\right)^5}{\lfloor 5} + \cdots\cdots \tag{35}$$

Again the q terms in this case involve only complete differentiation, which in operating on $\varepsilon^{\gamma t}$ changes the p to γ and therefore the q to s in equation (35) which gives

$$\frac{\operatorname{Sinh} q(l-x)}{ql}\varepsilon^{\gamma t} = \frac{\operatorname{Sinh} s(l-x)}{sl}\varepsilon^{\gamma t}. \tag{36}$$

Combining (34) and (36) we get for the following expression for the steady voltage on the line:

$$V_s = \frac{E \operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl}\varepsilon^{\gamma t}. \tag{37}$$

Replacing γ by $j\omega$, we have

$$V_s = \frac{E \operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl}\varepsilon^{j\omega t},$$
$$s^2 = (Lj\omega + R)(Cj\omega + g). \tag{38}$$

The above is the well-known solution for the steady state and is obvious from (10). The derivation of (38) is incidental, the main purpose of this paper being the study of the transient effects which occur during the establishment of the steady state. Referring to equations (12), (30) and (32), we find that remaining terms of the expansion $\frac{ql}{\operatorname{Sinh} ql}$ operated on $\varepsilon^{\gamma t}$ are as follows:

$$\left.\begin{aligned}\frac{ql}{\operatorname{Sinh} ql}\varepsilon^{\gamma t} = {} & -2q^2l^2\left\{\frac{v^2}{l^2(k_1 - k_1')}\left(\frac{\varepsilon^{k_1' t}}{\gamma - k_1'} - \frac{\varepsilon^{k_1 t}}{\gamma - k_1}\right)\right. \\ & - \frac{v^2}{l^2(k_2 - k_2')}\left(\frac{\varepsilon^{k_2' t}}{\gamma - k_2'} - \frac{\varepsilon^{k_2 t}}{\gamma - k_2}\right) \\ & + \frac{v^2}{l^2(k_3 - k_3')}\left(\frac{\varepsilon^{k_3' t}}{\gamma - k_3'} - \frac{\varepsilon^{k_3 t}}{\gamma - k_3}\right) \\ & \left. - \cdots\cdots\cdots\cdots\cdots\right\},\end{aligned}\right\} \tag{39}$$
$$(t)$$

and the above expression is again to be operated on by $E\,\frac{\text{Sinh}\,q\,(l-x)}{ql}$ to get the expression for V_t the transient voltage on the line. The term $\frac{\text{Sinh}\,q\,(l-x)}{q\,l}$ multiplied by q^2l^2, the factor in the right-hand side of equation (39), may be expressed in a series as follows:

$$\frac{q^2l^2\,\text{Sinh}\,q(l-x)}{ql} = q^2l^2\left(1-\frac{x}{l}\right)+\frac{q^4l^4}{\underline{|3}}\left(1-\frac{x}{l}\right)^3+\frac{q^6l^6}{\underline{|5}}\left(1-\frac{x}{l}\right)^5+\cdots\cdots \quad (40)$$

Operating by (40) on each one of the terms of (39) involves complete differentiation and will only change the p's in the q expression to k_1, k'_1, k_2, k'_2, k_3, k'_3, etc.

That is, operating by $ql\ \text{Sinh}\,q(l-x)$ on ε^{k_1t} gives

$$q\,l\,\text{Sinh}\,q(l-x)\varepsilon^{k_1t} = m_1 l\,\text{Sinh}\,m_1(l-x)\varepsilon^{k_1t}, \quad (41)$$

where

$$m_1^2 = \frac{1}{v^2}\left\{k_1^2+2k_1(a+b)+4ab\right\}. \quad (42)$$

Operating in the same way on all the other terms of equation (39), we get

$$\begin{aligned} V_t = -2E\frac{v^2}{l^2}\Bigg\{ &\frac{1}{k_1-k_1'}\left[\frac{m_1' l\,\text{Sinh}\,m_1'(l-x)}{\gamma-k_1'}\varepsilon^{k_1't}-\frac{m_1 l\,\text{Sinh}\,m_1(l-x)}{\gamma-k_1}\varepsilon^{k_1t}\right] \\ &-\frac{1}{k_2-k_2'}\left[\frac{m_2' l\,\text{Sinh}\,m_2'(l-x)}{\gamma-k_2'}\varepsilon^{k_2't}-\frac{m_2 l\,\text{Sinh}\,m_2(l-x)}{\gamma-k_2}\varepsilon^{k_2t}\right] \\ &+\frac{1}{k_3-k_3'}\left[\frac{m_3' l\,\text{Sinh}\,m_3'(l-x)}{\gamma-k_3'}\varepsilon^{k_3't}-\frac{m_3 l\,\text{Sinh}\,m_3(l-x)}{\gamma-k_3}\varepsilon^{k_3t}\right] \\ &-\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\Bigg\} \end{aligned} \quad (43)$$

The values of k_1, k'_1, k_2, k'_2, k_3, k'_3, etc., are given by equations (17) and (21) and may be put in the following form:

$$\left.\begin{aligned} k_1 &= -\alpha+j\beta_1, \\ k_1' &= -\alpha-j\beta_1, \\ k_2 &= -\alpha+j\beta_2, \\ k_2' &= -\alpha-j\beta_2, \\ &\cdots\cdots\cdots \\ k_n &= -\alpha+j\beta^n, \\ k'_n &= -\alpha-j\beta^n, \end{aligned}\right\} \quad (44)$$

where

$$\alpha = a+b$$

$$\beta_n = \sqrt{\left(\frac{n\pi v}{l}\right)^2-\left(a-b\right)^2} \quad (45)$$

Substituting for the value of k from (44) into (42), we get

$$m_1^2 = \frac{1}{v^2}\left\{\alpha^2 - \beta_1^2 - 2\alpha j\beta_1 - 2\alpha^2 + 2\alpha j\beta_1 + 4ab\right\}$$

$$= \frac{1}{v^2}\left\{-\alpha^2 - \beta_1^2 + 4ab\right\}$$

Substituting the values of α and β from (45), we get

$$m^2{}_1 = -\frac{\pi^2}{l^2}. \tag{46}$$

Similarly we find

$$\left.\begin{aligned} m^{2\prime}{}_1 &= -\frac{\pi^2}{l^2}, \\ m^2{}_2 = m^{2\prime}{}_2 &= -\left(\frac{2\pi}{l}\right)^2, \\ m^2{}_3 = m^{2\prime}{}_3 &= -\left(\frac{3\pi}{l}\right)^2, \\ &\cdots\cdots\cdots\cdots \end{aligned}\right\} \tag{47}$$

We also have

$$\left.\begin{aligned} k_1 - k_1' &= 2j\beta_1, \\ k_2 - k_2' &= 2j\beta_2, \\ &\cdots\cdots\cdots \\ k_n - k_n' &= 2j\beta_n. \end{aligned}\right\} \tag{48}$$

Substituting the values from (47) and (48) in (43) and using the relation

$$\mathrm{Sinh}\, jx = j\,\mathrm{Sin}\, x,$$

equation (43) reduces to the following:

$$\begin{aligned} V_t = -E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\Bigg\{ & \frac{\pi}{\beta_1} j\,\mathrm{Sin}\,\pi\left(1-\frac{x}{l}\right)\left[\frac{\varepsilon^{-j\beta_1 t}}{\gamma+\alpha+j\beta_1} - \frac{\varepsilon^{j\beta_1 t}}{\gamma+\alpha-j\beta_1}\right] \\ & - \frac{2\pi}{\beta_2} j\,\mathrm{Sin}\,2\pi\left(1-\frac{x}{l}\right)\left[\frac{\varepsilon^{-j\beta_2 t}}{\gamma+\alpha+j\beta_2} - \frac{\varepsilon^{j\beta_2 t}}{\gamma+\alpha-j\beta_2}\right] \\ & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ & \pm\frac{n\pi}{\beta_n} j\,\mathrm{Sin}\,n\pi\left(1-\frac{x}{l}\right)\left[\frac{\varepsilon^{-j\beta_n t}}{\gamma+\alpha+j\beta_n} - \frac{\varepsilon^{j\beta_n t}}{\gamma+\alpha-j\beta_n}\right]\Bigg\}. \end{aligned} \tag{49}$$

The above may be further simplified. Replacing γ by $j\omega$, we have

$$\begin{aligned} & \frac{\varepsilon^{-j\beta_1 t}}{\alpha+j(\omega+\beta_1)} - \frac{\varepsilon^{j\beta_1 t}}{\alpha+j(\omega-\beta)} \\ &= \frac{(\alpha+j\omega-j\beta_1)(\mathrm{Cos}\,\beta_1 t - j\,\mathrm{Sin}\,\beta_1 t) - (\alpha+j\omega+j\beta_1)(\mathrm{Cos}\,\beta_1 t + j\,\mathrm{Sin}\,\beta_1 t)}{(\alpha^2+\beta_1{}^2-\omega^2)+2j\omega\alpha} \\ &= \frac{2\left\{(\omega-\alpha j)\,\mathrm{Sin}\,\beta_1 t - j\beta_1\,\mathrm{Cos}\,\beta_1 t\right\}}{\alpha^2-\beta_1{}^2-\omega^2+2j\omega\alpha} \end{aligned}$$

Using only the imaginary part, so that when multiplied by the imaginary factor j in equation (49) will give the real part of (49), we get

$$\frac{\varepsilon^{-j\beta_1 t}}{\alpha + j\omega + j\beta_1} - \frac{\varepsilon^{j\beta_1 t}}{\alpha + j\omega - j\beta_1}\left(\begin{matrix}\text{imaginary}\\ \text{part}\end{matrix}\right) = \frac{j \operatorname{Sin}(\beta_1 t + \varphi_1)}{K_1}, \tag{50}$$

where

$$K_1 = \sqrt{\frac{(\alpha^2 + \beta_1^2 - \omega^2)^2 + 4\alpha^2\omega^2}{\alpha^2 + \beta_1^2}},$$
$$\operatorname{tau}\varphi_1 = \frac{\beta_1(\alpha^2 + \beta_1^2 - \omega^2)}{\alpha(\alpha^2 + \beta_1^2 + \omega^2)}, \tag{51}$$

and similar transformations for all the other terms in (49), using different β's; β_2, β_3, β_4, etc., for the other terms.

Substituting from (51) in (49), we finally get for V_t the transient voltage on the line

$$\begin{aligned} V_t = -E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\Big\{ & \frac{\pi}{\beta_1 K_1}\operatorname{Sin}\pi\left(1-\frac{x}{l}\right)\operatorname{Sin}(\beta_1 t + \varphi_1) \\ & -\frac{2\pi}{\beta_2 K_2}\operatorname{Sin}2\pi\left(1-\frac{x}{l}\right)\operatorname{Sin}(\beta_2 t + \varphi_2) \\ & +\frac{3\pi}{\beta_3 K_3}\operatorname{Sin}3\pi\left(1-\frac{x}{l}\right)\operatorname{Sin}(\beta_3 t + \varphi_3) \end{aligned} \tag{52}$$

or

$$- \cdots\cdots\cdots\cdots\cdots\Big\}$$

$$V_t = E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n\frac{n\pi}{\beta_n K_n}\operatorname{Sin}n\pi\left(1-\frac{x}{l}\right)\operatorname{Sin}(\beta_n t + \varphi_n). \tag{53}$$

Combining the above with equation (38) we get the complete expression for the voltage at any point on the line and at any time (t) after the application of the e.m.f. The component given by (38) represents the steady state, and the component given by (53) represents the transient state. The complete expression is

$$\begin{aligned} V = V_s + V_t = \frac{E\operatorname{Sinh}s(l-x)}{\operatorname{Sinh}sl}\varepsilon^{j\omega t} + E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n\frac{n\pi}{\beta_n K_n} \\ \operatorname{Sin}n\pi\left(1-\frac{x}{l}\right)\operatorname{Sin}(\beta_n t + \varphi_n). \end{aligned} \tag{54}$$

Only the real part of the first term of the right-hand member of above equation to be used.

The expression for the current distribution on the line is easily derived from (54) by the aid of either of equations (1). Use the second equation:

$$-\frac{dI}{dx} = C\frac{dV}{dt} + gV.$$

Using the expression for V given by (54), we have

$$
\begin{aligned}
-\frac{dI}{dx} &= (Cj\omega + g)\, E \frac{\operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl}\, \varepsilon^{j\omega t} \\
&+ CE\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n \frac{n\pi}{K_n}\operatorname{Sin} n\pi\left(1-\frac{x}{l}\right)\operatorname{Sin}(\beta_n t+\varphi_n) \\
&- CE\alpha\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n \frac{n\pi}{\beta_n K_n}\operatorname{Sin} n\pi\left(1-\frac{x}{l}\right)\operatorname{Sin}(\beta_n t+\varphi_n) \qquad (55) \\
&+ gE\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n \frac{n\pi}{\beta_n K_n}\operatorname{Sin} n\pi\left(1-\frac{x}{l}\right)\operatorname{Sin}(\beta_n t+\varphi_n).
\end{aligned}
$$

Combining the summation terms, we get

$$
\begin{aligned}
-\frac{dI}{dx} &= (Cj\omega+g)\frac{E\operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl}\varepsilon^{j\omega t} + E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n\frac{n\pi}{K_n}\operatorname{Sin} n\pi\left(1-\frac{x}{l}\right) \\
&\qquad\left\{C\cos(\beta_n t+\varphi_n)+\frac{(g-\alpha)}{\beta_n}\operatorname{Sin}(\beta_n t+\varphi_n)\right\} \\
&= (Cj\omega+g)\,E\frac{\operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl}\varepsilon^{j\omega t} + E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n\frac{n\pi}{K_n}\sqrt{C^2+\frac{(g-C\alpha)^2}{\beta^2}} \\
&\qquad \operatorname{Sin} n\pi\left(1-\frac{x}{l}\right)\operatorname{Cos}(\beta_n t+\varphi_n-\psi_n). \qquad (56) \\
&\qquad \tan\psi_n = \frac{g-\alpha C}{\beta_n}.
\end{aligned}
$$

Integrating the above with respect to x, we get the expression for the current on the line as follows:

$$
\begin{aligned}
I &= \frac{Cj\omega+g}{s}\,\frac{E\operatorname{Cosh} s(l-x)}{\operatorname{Sinh} sl}\varepsilon^{j\omega t} - E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n\frac{l}{K_n}\sqrt{C^2+\frac{(g-\alpha)^2}{\beta_n^2}} \\
&\qquad \operatorname{Cos} n\pi\left(1-\frac{x}{l}\right)\operatorname{Cos}(\beta_n t+\varphi_n-\psi_n). \qquad (57)
\end{aligned}
$$

The above equations (54) and (57) are the general expressions for the voltage and current distribution on the line for an impressed electromotive force of any frequency, one component in the expressions giving the steady state voltage and current on the line, and the other the transient voltage and current, the latter subsiding exponentially. Consider now special cases.

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For a constant e.m.f. zero frequency, we have $s^2 = Rg$, which is an extremely small quantity, and we may therefore write:

$$
\frac{\operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl} = \frac{s(l-x)}{sl} = 1-\frac{x}{l}. \qquad (58)
$$

Also by (51) putting $\omega = 0$, we have

$$\left.\begin{aligned} K_1 = K_2 = K_3 = \cdots \cdots K_n &= \sqrt{\alpha^2 + \beta^2} \\ \tan \varphi_n &= \frac{\beta_n}{\alpha} \end{aligned}\right\} \tag{59}$$

Substituting in (54) and (57), we get

$$V = V_s + V_t = E\left(1 - \frac{x}{l}\right) +$$

$$E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n \frac{n\pi}{\beta_n} \operatorname{Sin} n\pi\left(1 - \frac{x}{l}\right) \operatorname{Sin}(\beta_n t + \varphi_n). \tag{60}$$

$$I = E\sqrt{\frac{g}{R}}\frac{\operatorname{Cosh} s(l-x)}{\operatorname{Sinh} s\, l} - E\frac{v^2}{l^2}\varepsilon^{-\alpha t}$$

$$\sum_{n=1}^{n=\infty}(-1)^n l\sqrt{\frac{C^2 + \frac{(g-\alpha C)^2}{\beta_n^2}}{K_n}} \operatorname{Cos} n\pi\left(1 - \frac{x}{l}\right) \operatorname{Cos}(\beta_n t + \varphi_n - \psi_n) \tag{61}$$

when g is very small

$$\frac{\operatorname{Cosh} s(l-x)}{\operatorname{Sinh} sl} = \frac{1}{sl} = \frac{1}{\sqrt{Rgl}}$$

and the above reduces to

$$I = \frac{E}{Rl} - E\frac{v^2}{l^2}\varepsilon^{-\alpha t}\sum_{n=1}^{n=\infty}(-1)^n l\sqrt{\frac{C^2 + \frac{(g-\alpha C)^2}{\beta_n^2}}{K_n}} \operatorname{Cos} n\pi\left(1 - \frac{x}{l}\right) \operatorname{Cos}(\beta_n t + \varphi_n - \psi_n). \tag{62}$$

In equations (54), (57), (60) and (61) the factor

$$\varepsilon^{-\alpha t} = \varepsilon^{-\frac{1}{2}\left(\frac{R}{L} + \frac{g}{C}\right)t}$$

determines the time rate at which the transient components of the voltage and current die out.

OCEAN CABLE.

From equations (54) and (57) the expressions for the voltage and current distribution on an ocean telegraph cable may be readily derived. In an ocean cable the inductance and leakage are negligible, it is assumed that $L = o$ and $g = o$. In this case we have by (21),

$$k_n = -a + \sqrt{a^2 - \frac{n^2\pi^2v^2}{l^2}},$$

$$k'_n = -a - \sqrt{a^2 - \frac{n^2\pi^2v^2}{l^2}}, \tag{63}$$

$$a^2 = \frac{R^2}{4L^2}, v^2 = \frac{1}{LC}.$$

For negligible inductance a^2 is very large in comparison with $\frac{\pi^2 v^2}{l^2}$, and we may therefore put

$$k_n = -a + a\left(1 - \frac{n^2\pi^2v^2}{l^2}\right)^{1/2} = -a + a\left(1 - \frac{1}{2}\frac{n^2\pi^2v^2}{a^2l^2}\right)$$

$$= -\frac{1}{2}\frac{n^2\pi^2v^2}{al^2} = -\frac{n^2\pi^2}{RCl^2}. \tag{64}$$

Similarly

$$k'_n = -a - a\left(1 - \frac{1}{2}\frac{n^2\pi^2v^2}{a^2l^2}\right)^4 = 2a = -\infty \text{ for } L = 0 \tag{65}$$

and $$\varepsilon^{k'nt} = 0$$

Also $k_1, k_2 \ldots k_n$, etc., are negligible in comparison with $k'_1, k'_2 \ldots k'_n$, etc., respectively.

Substituting the values from above equations in (43), we have

$$V_t = -\frac{2E}{2a}\frac{v^2}{l^2}\left\{\frac{-m_1 l \operatorname{Sinh} m_1(l-x)}{\gamma - k_1}\varepsilon^{-\frac{\pi^2}{RCl^2}t} + \frac{m_2 l \operatorname{Sinh} m_2(l-x)}{\gamma - k_2}\varepsilon^{-\frac{(2\pi)^2}{RCl^2}t}\right.$$

$$\left. - \frac{m_3 l \operatorname{Sinh} m_3(l-x)}{\gamma - k_3}\varepsilon^{-\frac{(3\pi)^2}{RCl^2}t} + \cdots\cdots\right\} \tag{66}$$

Replacing m_1, m_2, m_3, etc., by the corresponding values $j\frac{\pi}{l}$, $j\frac{2\pi}{l}$, $j\frac{3\pi}{l}$, etc., and γ by $j\omega$, the above becomes

$$V_t = -\frac{2E}{RCl^2}\left\{\frac{\pi \operatorname{Sin}\pi\left(1-\frac{x}{l}\right)}{j\omega + \frac{\pi^2}{RCl^2}}\varepsilon^{-\frac{\pi^2}{RCl^2}t} - \frac{2\pi \operatorname{Sin} 2\pi\left(1-\frac{x}{l}\right)}{j\omega + \frac{(2\pi)^2}{RCl^2}}\varepsilon^{-\frac{(2\pi)^2}{RCl^2}t} + \cdots\right\}$$

$$= \frac{2E\pi}{RCl^2}\sum_{n=1}^{n=\infty}(-1)^n \frac{n \operatorname{Sin} n\pi\left(1-\frac{x}{l}\right)}{j\omega + \frac{(n\pi)^2}{RCl^2}}\varepsilon^{-\frac{(n\pi)^2}{RCl^2}t} \tag{67}$$

For the steady state we have by (38)

$$V_s = \frac{E \operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl}\varepsilon^{j\omega t},$$

but in this case

$$s^2 = RCj\omega.$$

The complete expression for the voltage on the cable for a sinusoidal e.m.f. of frequency $\frac{\omega}{2\pi}$ impressed on the cable is

$$V = V_s + V_t = E\frac{\operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl}\varepsilon^{j\omega t} + \frac{2E\pi}{RCl^2}\sum_{n=1}^{n=\infty}(-1)^n \frac{n \operatorname{Sin} n\pi\left(1-\frac{x}{l}\right)}{j\omega + \frac{(n\pi)^2}{RCl^2}}\varepsilon^{-\frac{(n\pi)^2 t}{RCl^2}}. \tag{68}$$

The expression for the current on the cable may be derived in similar manner from equation (57), but can be more directly obtained from (68). For $L = o$, we have the relation

$$RI = -\frac{dV}{dx},$$

and

$$I = \frac{Es}{R}\frac{\operatorname{Cosh} s(l-x)}{\operatorname{Sinh} sl}\varepsilon^{j\omega t} - \frac{2E\pi^2}{RCl^2}\sum_{n=1}^{n=\infty}(-1)^n \frac{n^2 \operatorname{Cos} n\pi\left(1-\frac{x}{l}\right)}{Rl\left(j\omega + \frac{(n\pi)^2}{RCl^2}\right)}\varepsilon^{-\frac{(n\pi)^2 t}{RCl^2}} \tag{69}$$

For a constant e.m.f., $\omega = o$

$$\frac{\operatorname{Sinh} s(l-x)}{\operatorname{Sinh} sl} = 1 - \frac{x}{l}, \quad \frac{\operatorname{Cosh} s(l-x)}{\operatorname{Sinh} sl} = \frac{1}{sl}$$

and equations (68) and (69) reduce to

$$V = E\left(1-\frac{x}{l}\right) + 2E\sum_{n=1}^{n=\infty}(-1)^n \frac{\operatorname{Sin} n\pi\left(1-\frac{x}{l}\right)}{n\pi}\varepsilon^{-\frac{(n\pi)^2 t}{RCl^2}} \tag{70}$$

$$I = \frac{E}{Rl} - \frac{2E}{Rl}\sum_{n=1}^{n=\infty}(-1)^n \operatorname{Cos} n\pi\left(1-\frac{x}{l}\right)\varepsilon^{-\frac{(n\pi)^2 t}{RCl^2}}. \tag{71}$$

Equations (70) and (71) are the well-known solutions of the telegraphic equation which was first given by Lord Kelvin in 1855 and has since been studied by other investigators. It is seen that by the use of the method developed in this paper, the solution of the telegraphic equation is but a special case of the general solution given by equations (54) and (57). Even for the cable telegraph problem we have by this method arrived at a more comprehensive solution, equations (68) and (69), which are applicable for alternating and direct voltages, reducing to (70) and (71) when the frequency is zero.

THE CRYSTAL STRUCTURE OF BISMUTH.*

BY

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THE electrical and magnetic properties of metallic bismuth are in many respects so peculiar that an exact knowledge of its crystal structure seems important in any attempt to correlate these properties for metals in general. The work of previous investigators of the structure has accordingly been reviewed, and some additional data obtained as opportunity offered.

The spectrometric method was used by Ogg,[1] who obtained reflections of palladium X-rays from the (111) and (200) planes, and by James,[2] who obtained reflections of rhodium X-rays from the same planes and from the $(11\bar{1})$ planes in addition. The nomenclature of planes depends upon the choice of crystallographic axes, and both of the investigators referred to employed rhombohedral axes mutually inclined at 87°–34′, as given by the standard handbooks of crystallography. With this choice of axes the units of structure are face-centred rhombohedra which differ but little from cubes. Two such lattices must be present, and are so situated with respect to each other that the whole array of points is not much different from a simple cubic lattice.

The face-centred rhombohedral space-lattice is not, however, recognized as a fundamental type. Simplicity in nomenclature is attained by using instead of the above-described axes a set of rhombohedral axes which are halves of the face-diagonals of the rhombohedron first chosen, and which are therefore mutually inclined at 57°–16′. The corresponding space-lattice is simple rhombohedral, a fundamental type (Γ_{rh}). It will be noticed that the longest body diagonal of a cell of either of these space-lattices has the same length. Quantities and symbols referred to the simpler axes will be indicated in what follows by the use of primes. Formulæ for transforming the indices of planes have been given

* Communicated by Gen. John J. Carty, E.D., Associate Editor of this JOURNAL.

[1] A. Ogg, *Phil. Mag.*, (6), **42**, 163–166, July, 1921.

[2] R. W. James, *Phil. Mag.*, (6), **42**, 193–196, July, 1921.

by Wyckoff [3] who was forced to use a similar artifice in analyzing the structure of calcite.

Table I summarizes the data referred to above, and the results computed from currently accepted X-ray wave-lengths.[4] The results are seen to be in as good agreement as the indicated accuracy in angular measurements would lead one to expect. The mean value

$$a = 6.546 \times 10^{-8} \text{ cm.} \quad (a' = 4.726 \times 10^{-8} \text{ cm.})$$

corresponds to a density of 9.863 gm./cm.^{3} which is not unreason-

TABLE I.

Observer X-rays of Effective Wave-length[4]		Ogg[1] Palladium 0.588 × 10^{-8}cm. 10^8 ×			James[2] Rhodium 0.614 × 10^{-8} cm. 10^8 ×		
Planes		θ	a	a'	θ	a	a'
(111)	(111)′	4°-18′	6.520	4.708	4°-29′	6.531	4.715
(11$\bar{1}$)	(100)′				4°-45′	6.519	4.707
(200)	(110)′	5°-08′	6.583	4.753	5°-25′	6.516	4.704
(222)	(222)′				8°-54′	6.600	4.765
(22$\bar{2}$)	(200)′				9°-27′	6.576	4.748
(400)	(220)′				10°-52′	6.525	4.711
(333)	(333)′				13°-26′	6.592	4.759
(600)	(330)′				16°-20′	6.497	4.690
Mean values			6.55	4.73		6.544	4.725

[1] A. Ogg, *Phil. Mag.*, (6), **42**, 163-166, July, 1921.
[2] R. W. James, *Phil. Mag.*, (6), **42**, 193-196, July, 1921.
[4] W. Duane, *Nat. Res. Counc. Bull.*, **1**, 383-408, Nov., 1920.

ably high, considering the improbability of perfect fit between the individual crystallites in massive samples.[5]

James found that the points of one lattice lie on the trigonal axes through the points of the other, not quite at the centres of the rhombohedra. Recalculating from his data his result is confirmed, the ratio of intensities for the first three orders of reflection from the (111) planes agreeing with a displacement of either lattice from the body-centred position in the other by $(0.306 \pm 0.033) \times 10^{-8}$ cm. In terms of the two sets of axes

[3] R. W. G. Wyckoff, *Amer. Jour. Sci.*, (4), **50**, 317–360, Nov., 1920.
[4] W. Duane, *Nat. Res. Counc. Bull.*, **1**, 383–408, Nov., 1920.
[5] The density is calculated from $a' = 4.726 \times 10^{-8}$ cm., $a' = 57° - 16'$, using the following constants: atomic weight of bismuth, 209.0; number of molecules per gram molecule, 6.0594×10^{23}, the latter being taken from Birge, *Phys. Rev.*, (2), **14**, 365, (1919).

TABLE II.

Film No.	90	96	102	105	130	147	152	159	225	407
$s =$	3.60									
								3.62		
	4.14									
	4.24									
	4.34									
		4.35								
		4.36								
							4.39	4.39		4.39
						4.42				
		4.44	4.44	4.44						
					4.45					
		5.90								
	6.00									
										6.02
								6.06		
							6.11		6.11	
			6.12							
						6.14				
								6.32		
				6.36						
										6.37
			6.38							
									6.39	
					6.45					
	7.10									
							7.13			
								7.30		
							7.34			
		7.38								
									7.39	
						7.40				
	7.51									
		7.57								
								7.71		
										7.76
				7.80						
								8.83		
										8.85
							8.86			
			8.88							
						8.89				
				8.91						
	9.25									
								9.30		
						9.31				
	9.38									
		9.40								
	9.55									
								9.72		
										9.74
							9.75			
	9.84									
										10.07
							10.10			
		10.14		10.14						
					10.20					

TABLE II (*Continued*).

Film No.	90	96	102	105	130	147	152	159	225	407
$s =$		10.50						10.50		
							10.52			
		10.58								
										10.93
								10.95		
							10.97			
	11.10									
		11.12								
				11.19						
		11.52								
		12.80								
							12.86	12.86		
		12.88								
				12.91						
	13.12									
	14.00									
				14.08						
	14.20									
		15.14		15.14′						
		15.34								
	15.69									
	17.03									
	18.31									
	20.10									
	20.77									
	21.90									
	24.29									

the representative points, those absorbed by a single rhombohedron, are accordingly:

$$(0, 0, 0),\ (\tfrac{1}{2}, \tfrac{1}{2}, 0),\ (\tfrac{1}{2}, 0, \tfrac{1}{2}),\ (0, \tfrac{1}{2}, \tfrac{1}{2}),\ \text{and}$$
$$(u, u, u),\ (u + \tfrac{1}{2}, u + \tfrac{1}{2}, u),\ (u + \tfrac{1}{2}, u, u + \tfrac{1}{2}),\ (u, u + \tfrac{1}{2}, u + \tfrac{1}{2});$$

or

$$(0, 0, 0)',\ \text{and}\ (u, u, u)'.\quad \text{In either case } u = 0.474 \pm 0.003.$$

New data were taken by the powder method, using X-rays of molybdenum, and only the larger crystals of the ground samples seemed to be sufficiently perfect to give good reflections, so that the photographs obtained consisted of widely separated spots, many possible reflections not being observed at all. The data are summarized in Table II. Under these conditions the most direct way of comparing the new data with the old was to calculate the position, s, and intensity, i, of the reflections to be expected from a random distribution of crystals having the previously determined structure, and to compare the position and frequency of occurrence of spots on the new photographs with this expected

TABLE III.

(hkl)	$(hkl)'$	$\log (d \times 10^8)$	s	i
111	111	0.59518	3.69	88
$11\bar{1}$	100	0.57085	3.90	9
200	110	0.51421	4.44	1000
220	211	0.37275	6.17	480
$20\bar{2}$	$10\bar{1}$	0.35501	6.43	493
311	221	0.30613	7.20	62
222	222	0.29415	7.40	290
$31\bar{1}$	210	0.29294	7.43	22
$31\bar{1}$	$11\bar{1}$	0.28663	7.54	2
$22\bar{2}$	200	0.26982	7.84	324
200	220	0.21319	8.94	230
$33\bar{1}$	322	0.19033	9.44	68
$33\bar{1}$	311	0.17869	9.70	35
420	321	0.17194	9.85	165
$31\bar{3}$	$20\bar{1}$	0.16763	9.95	1
$40\bar{2}$	$21\bar{1}$	0.15775	10.19	194
422	332	0.14044	10.61	116
$42\bar{2}$	310	0.12220	11.08	151
$33\bar{3}$	$33\bar{3}$	0.11806	11.19	75
422	$21\bar{1}$	0.11645	11.23	164
$51\bar{1}$	331	0.10691	11.49	46
$51\bar{1}$	320	0.09891	11.70	24
$51\bar{1}$	$22\bar{1}$	0.09373	11.85	9
$33\bar{3}$	300	0.09375	11.85	9
440	422	0.07172	12.49	84
$53\bar{1}$	$43\bar{2}$	0.05519	12.99	56
$40\bar{4}$	$20\bar{2}$	0.05397	13.02	123
$44\bar{2}$	433	0.05345	13.04	58
$53\bar{1}$	421	0.04679	13.25	35
600	330	0.03709	13.56	89
$44\bar{2}$	$41\bar{1}$	0.03709	13.56	89
$51\bar{3}$	$31\bar{1}$	0.03672	13.57	7
$51\bar{3}$	$21\bar{2}$	0.03476	13.63	1
424	$30\bar{1}$	0.02935	13.81	107
620	431	0.01960	14.14	66
$53\bar{3}$	$44\bar{3}$	0.01522	14.29	63
$60\bar{2}$	$32\bar{1}$	0.00896	14.50	90
$62\bar{2}$	442	0.00511	14.64	46
$53\bar{3}$	410	9.99483	15.01	15
$44\bar{4}$	444	9.99312	15.07	29
$62\bar{2}$	420	9.99191	15.11	72
$53\bar{3}$	$31\bar{1}$	9.99001	15.18	1
$62\bar{2}$	$22\bar{2}$	9.98560	15.34	88
$55\bar{1}$	533	9.97398	15.78	52
$44\bar{4}$	400	9.96879	15.98	75
$71\bar{1}$	441	9.96674	16.06	37
$55\bar{1}$	522	9.96674	16.06	37
640	532	9.96558	16.11	38
$71\bar{1}$	$43\bar{0}$	9.96111	16.28	24
$71\bar{1}$	$33\bar{1}$	9.95699	16.45	12
$64\bar{2}$	$54\bar{3}$	9.95555	16.50	24
$51\bar{5}$	$30\bar{2}$	9.95293	16.61	1
$60\bar{4}$	$31\bar{2}$	9.94921	16.76	74
$55\bar{3}$	544	9.94701	16.85	57
$64\bar{2}$	521	9.94242	17.04	47

TABLE III (*Continued*).

(hkl)	$(hkl)'$	$\log (d \times 10^8)$	s	i
$73\bar{1}$	$54\bar{2}$	9.93934	17.17	45
$62\bar{4}$	$41\bar{1}$	9.93491	17.36	64
$73\bar{1}$	$53\bar{1}$	9.93315	17.44	32
$62\bar{4}$	$31\bar{2}$	9.93246	17.46	70
$55\bar{3}$	$51\bar{1}$	9.92832	17.65	20
$71\bar{3}$	$42\bar{1}$	9.92477	17.80	11
$71\bar{3}$	$32\bar{2}$	9.92243	17.90	4
$53\bar{5}$	$40\bar{1}$	9.92243	17.90	4
644	554	9.91635	18.17	11
733	553	9.91614	18.18	50
800	440	9.91215	18.36	40
820	541	9.90320	18.77	29
$73\bar{3}$	520	9.89983	18.93	18
555	555	9.89621	19.10	53
$88\bar{2}$	$55\bar{2}$	9.89563	19.13	18
$66\bar{0}$	$63\bar{3}$	9.89563	19.13	18
$80\bar{2}$	$45\bar{1}$	9.89485	19.17	46
$64\bar{4}$	$51\bar{0}$	9.89485	19.17	46
$73\bar{3}$	$32\bar{2}$	9.89365	19.23	0
$64\bar{4}$	$41\bar{1}$	9.89080	19.36	57
662	644	9.88931	19.43	10
$75\bar{1}$	643	9.88912	19.44	44
$82\bar{2}$	530	9.88559	19.62	36
$75\bar{1}$	$63\bar{2}$	9.88322	19.73	34
$82\bar{2}$	$33\bar{2}$	9.87979	19.90	50
$60\bar{6}$	$30\bar{3}$	9.87789	20.00	55
$66\bar{2}$	622	9.87765	20.01	26
$55\bar{5}$	500	9.87188	20.30	8

distribution of reflections. Table III contains the results of such calculations for the particular apparatus employed, the reduction from the logarithm of the parameter of a set of planes to the length in centimetres of the arc of deviation involving the wave-length of the X-rays, 0.712×10^{-8} cm. (palladium $K\alpha_1$) and the radius of the film-holder, 20.36 cm. The calculations are carried out for all plane-spacings and orders of reflection which could give reflected spots within about twenty centimetres of the undeflected spot.[6]

The results contained in Tables II and III are better exhibited for comparison in Fig. 1, where the abscissa is the arc length, s, in centimetres. Vertical lines of a length proportional to the intensities given in Table III are drawn at the appropriate values of s, and the locations of spots listed in Table II are indicated by dots, those on any horizontal line belonging to a single photograph.

[6] The intensity if proportional to $\cos^2 \pi u (h+k+l)'$. Cf. R. W. G. Wyckoff, *loc. cit.*[3]

The complexity of the expected pattern makes an interpretation of the observed discrepancies somewhat difficult. It can be stated, however, that the structure of a single lattice is checked better

FIG. 1.

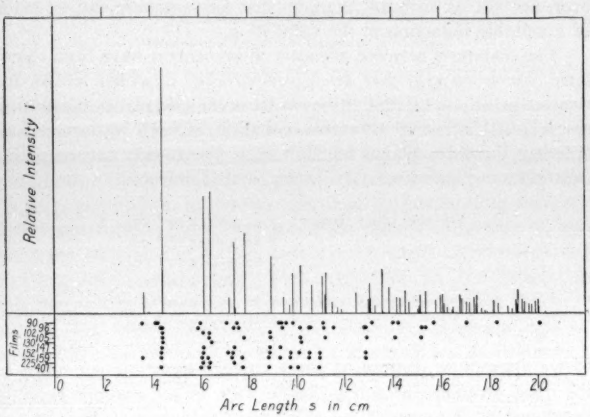
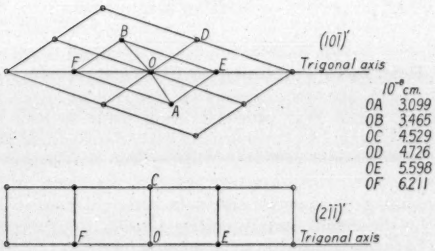


FIG. 2.



by the location of the photographic spots, which tend to fall short rather than to fall beyond the expected positions,[7] than is the relative position of the two lattices by the frequency of occurrence

[7] L. W. McKeehan, JOUR. FRANK. INST., **193**, 231–242, Feb., 1922.

of reflection from certain planes. In particular, the appearance of spots attributable to the planes $(221)'$ and $(311)'$, and the absence of any attributable to $(422)'$, $(330)'$ and $(411)'$, suggests that the bismuth atoms are not as uniformly spaced along the trigonal axis as the value $u = 0.474$ requires. The new data, however, are not of such an accuracy that any estimate can be made of a suitable reduction in the value of u.

The distances between adjacent atom-centres have been calculated for $u = 0.474$, and are given in Fig. 2 which shows the relative positions of the lattice-points on simple planes containing the trigonal axis and therefore common to both lattices. Considering the three planes of each type, the twenty lattice points nearest to any point we may select, lie as follows:

Of the other lattice:	3 at 3.099×10^{-8} cm.
	3 at 3.465×10^{-8} cm.
	1 at 5.598×10^{-8} cm.
	1 at 6.211×10^{-8} cm.
Of the same lattice:	6 at 4.529×10^{-8} cm.
	6 at 4.726×10^{-8} cm.

If we attempt to dispose of three valence electrons per atom in the most symmetrical and probable way, in the manner recently developed by Thomson,[8] we will find that they may best be put between the closest atom pairs, those separated by less than 3.5×10^{-8} cm. No attempt has been made to calculate the stability or other properties of such an arrangement.

Early References Pertaining to Chemical Warfare have been collected by C. A. Browne (*Jour. Ind. Eng. Chem.*, 1922, xiv, 646). During the Crimean War proposals were made to load incendiary shells with a solution of phosphorus in carbon disulphide and to load gas shells with cacodyl cyanide. During the Napoleonic Wars, an attempt was made to manufacture infernal machines or incendiary bombs containing phosphorus and potassium chlorate. Gunpowder was used by the Arabs and Byzantine Greeks for rockets and fire balls; the Germans applied it for loading fire-arms. Greek fire was probably a mixture of naphtha and quicklime with a certain amount of sulphur and pitch; when this mixture is wet with water, the hydration of the quicklime evolves sufficient heat to ignite the naphtha and other ingredients. J. S. H.

[8] J. J. Thomson, *Phil. Mag.*, (6), **43**, 721–757, April, 1922.

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

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Department of Chemistry, University of Chicago.

68. EXPERIMENTS ON THE SEPARATION OF MERCURY INTO ISOTOPES.

THE first isotopic material obtained in appreciable quantities was secured by Harkins and Broeker, who separated chlorine, as announced in February, 1920. Eight months later Broensted and Hevesy announced a separation of a much smaller magnitude, 50 parts per million in density, obtained by evaporating mercury at low pressures. Later they secured a density difference of 490 parts per million, but obtained only very small fractions of 0.2 and 0.3 cubic centimetre. The magnitude of the separation obtained in this laboratory is undoubtedly greater when the large size of the fractions is taken into account. The methods of separation used in this laboratory for mercury are as follows:

Method 1. Diffusion through filter paper at low pressures (Doctor Mulliken).
Method 2. (*a*) Evaporation at low pressures (Mulliken and Harkins, and Harkins and Madorsky).
(*b*) Distillation at very low pressures (Mulliken and Harkins).
Method 3. Methods 1 and 2*a* combined in one operation, but with the diffusion through filter paper as the principal process. Evaporative-diffusion (Doctor Mulliken.)

These three methods will be described in the following sections, but it may be stated that the combination method seems to give the most promise where an extensive separation is desired.

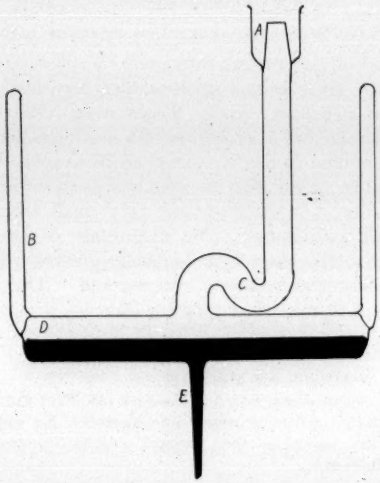
69. SEPARATION OF THE ISOTOPES OF MERCURY BY EVAPORATION AT LOW PRESSURES.

Only the purest mercury was used in this work, as is evident from the extensive study described later as made by Doctor Mulliken on the purification of mercury. Fig. 31 shows the design of an extremely efficient apparatus in which the molecules have to travel only about 5 mm. from the liquid surface before they condense on the roof (*R*), which is cooled with liquid air, or with carbon dioxide snow in toluene. Fig. 32 gives a slightly less efficient apparatus in which the use of liquid air

* Concluded from page 814, vol. 194, December, 1922.

is unnecessary, the chamber *C* being filled with ice and water. The molecules which condense on the lower part of the roof *C* gather in drops, and these roll down the roof and collect in the annular catch *D*, since the slope of this roof is made sufficiently steep so that drops of mercury will adhere to it. Thus the

FIG. 31.



Efficient form of evaporator for the separation of mercury into isotopes.

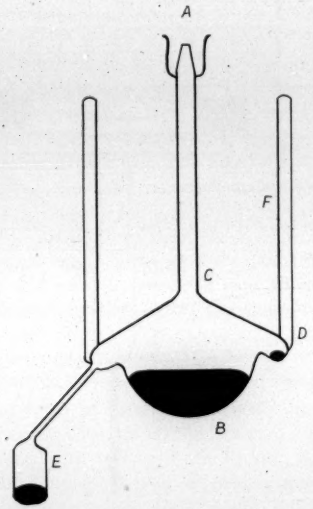
light fraction collects in *E*, while the heavy fraction remains in the chamber *B*.

The apparatus was filled through *A* and emptied by cutting off *E*,[92] containing the condensate, and then pouring the residue out through the opening. The ground-glass joint *A* was connected to a mercury diffusion pump and oil pump, and to a McLeod gage. During the runs the apparatus was evacuated to a pressure of 10^{-4} to 10^{-5} mm. The efficiency was probably not much reduced until the pressure rose to about 10^{-3} mm., when the presence of air caused a considerable slowing up of the opera-

[92] If a mercury-sealed stopcock is put at the bottom of *E*, the fractions which collect in *E* can be run out into an evacuated vessel at any time. This has been done in the later work.

tion, and some of the mercury molecules were then deflected so that they condensed on the roof of *D*. A difference in density of 133 parts per million, and in atomic weight of 0.027 unit was obtained very quickly, but no attempt was made to obtain a larger separation in this apparatus, since the work of the laboratory was for a year focussed upon a general survey of the efficiency of various processes of separating isotopes. By the use of this

FIG. 32.



Cross-section of evaporator.

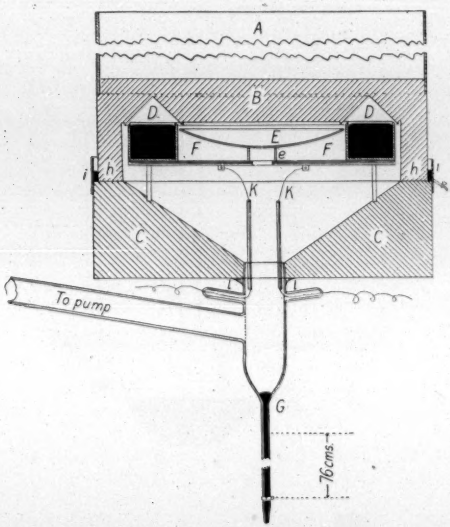
apparatus it was found that the separation coefficient for mercury is equal to 0.0057, but a later careful study by Doctor Mulliken showed that it is more nearly 0.0063, at least for diffusion through filter paper, as it is given in Table XLI.

70. SEPARATION OF THE ISOTOPES OF MERCURY BY EVAPORATION AT LOW PRESSURES IN A LARGE STEEL APPARATUS.

The apparatus described in the last section, since it is constructed of glass, cannot be made so that it gives a very large mercury surface in a vacuum, so a somewhat similar steel apparatus, which may be built with almost any desired surface, has been

designed by Mr. S. L. Madorsky and the writer. Fig. 33 shows a vertical section of such an apparatus, the trough of which will hold 2600 grams of mercury, while Fig. 34 shows the design of a similar apparatus to hold 11,500 grams. The former apparatus gives an efficiency of about 81 per cent. in terms of Mulliken's coefficient when operated at a rate of 25 c.c. per hour.

FIG. 33.



Steel apparatus for the separation of mercury into isotopes by vaporization. *A*, cylinder for ice; *B*, circular condensing roof, made of steel; *CC*, drain for the light fractions, made of steel; *DD*, annular steel trough holding 190 c.c. of mercury; *E*, watch glass with hole in centre, supported on a short glass tube, *e*; *FF*, heating element made of calorized wire and supported on glass rods; *G*, collecting tube made of glass; *hh*, ground joint; *ii*, mercury seal; *kk*, platinum wires; *ll*, ground joint and sealing wax.

The latter apparatus is in process of construction, so its efficiency has not been tested, but it should be about the same with a rate of evaporation of 50 c.c. per hour, at least at the beginning of the run.

The roof, the base, and the trough of the apparatus were cut from three steel forgings. Cast steel was not used since it is more liable to exhibit leaks and to give off large amounts of gas. The mercury is vaporized from the steel trough *D* while the

pressure of air in the apparatus is kept between 0.0001 and 0.001 mm. pressure. In the smaller apparatus the trough rests upon an iron plate in which is embedded a calorized nichrome resistance wire F, insulated by magnesium oxide surrounded by an iron sheath. In the larger apparatus the heating wire lies inside the mercury in the trough, but in contact with the bottom of the latter. The supports (f) on which the trough rests are made from glass or porcelain rods. The electric current is carried to the heating coil by two heavy platinum wires (i) sealed into the walls of the glass tube (G),* which serves to lead to the pump, and to drain off the mercury as it condenses. The platinum wires are insulated by two glass or porcelain tubes (l). The glass tube (G) is connected with the steel tube (S) by a ground, mercury sealed joint, as shown in Fig. 34. The direct connection with the lower steel disc, as shown in Fig. 33, has been abandoned, though it gives good service, since the mercury-sealed joint is easier to detach. The large ground joint (h), between the roof and the base of the apparatus, is kept tight by a mercury seal (i), the mercury of which is kept in place by a thin steel band. The slope of the roof above D is 45°, which is sufficiently steep to cause the drops of mercury to slide down the slope, rather than drop back into the trough.

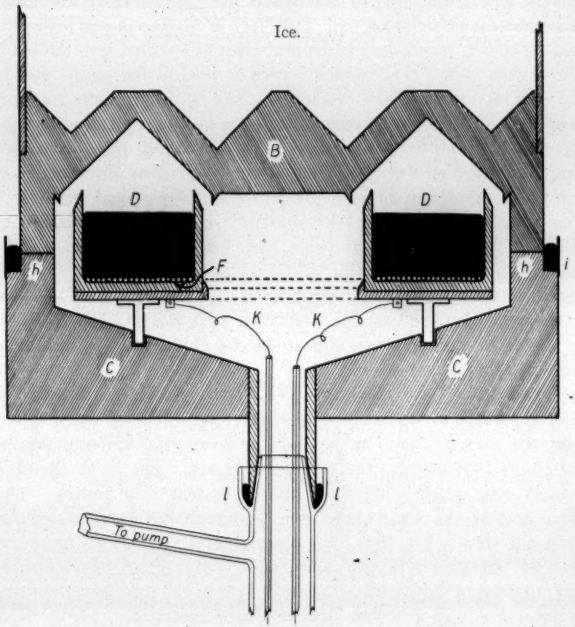
Operation of the Apparatus.—The trough of the thoroughly clean apparatus is filled with purest mercury, the roof fitted to the base, the mercury run in around the joint, the vacuum pumps started, and the current turned on the heater. The large chamber A is at once filled with sufficient ice to last four hours. The lower end of the long glass tube G, which has been sealed off below the stopcock with a long point, begins to fill with mercury. This has an atomic weight 0.006 unit lower than ordinary mercury, that is the liquid which collects first in the tube has a density 30 parts per million lower than ordinary mercury.

The molecules which escape from the surface of the trough (D) travel a distance of only from 1 to 2.5 cm. before they strike the cold roof (R), provided the trough is full and that they move vertically upward. While this distance is many times the mean free path of the molecules, the high efficiency obtained (81 per cent.) indicates that not over 19 per cent. of the mole-

* The apparatus shown in Fig. 34 has now been modified so that these platinum wires pass through insulating plugs in the steel base.

cules return to the evaporating surface. The rapidly moving unidirectional stream of mercury molecules from the hot surface (100° to 15° C.) to the cold surface serves to almost entirely prevent such a return. In the larger apparatus a *few* of the molecules must move 3 cm. upward from the full trough before they

FIG. 34.



Large steel apparatus of 850 c.c. capacity for the separation of mercury into isotopes (Harkins). The significance of the lettering is the same as given under Fig. 33.

strike the roof. As the evaporation proceeds the distance increases, and this decreases slightly the efficiency toward the end of the run.

Table XLII shows the results obtained in an average run with the smaller apparatus, starting with mercury of the ordinary atomic weight. As soon as it is completed the large apparatus

will be used for all of the work in which ordinary mercury is fractionated.

TABLE XLII.

Fractionation Scheme for 190 c.c., or 2600 gram Samples of Ordinary Atomic Weight.

Fraction.	Per cent.	C.C.	Weight.	Cut C or C_2-C_1.	Change of Density in Parts per Million. 90 per cent.	81 per cent.	Actual.	Change of Atomic Weight. 190 per cent.	Actual.
1	20	38	520	1.25	−25.4	−22.9	−22.8	−0.005	−0.0046
2	20	38	520	1.66−1.25	−18.2	−16.4		−0.0036	
3	15	28.5	390	2.22−1.66	−10.2	− 9.2		−0.0020	
4	15	28.5	390	3.33−2.22	− 0.4	− 0.36		−0.00008	
5	10	19	260	5 −3.33	+10.9	+ 9.8		+0.0022	
6	10	19	260	10 −5	+26.2	+23.6		+0.0052	
7	5	9.5	130	20 −10	+45.9	+41.3		+0.0092	
8	5	9.5	130	20	+85.2	+76.7	+78	+0.017	+0.016

The light fractions thus produced were refractionated as follows:

TABLE XLIII.

Fractionation Scheme for the Light Fractions of Table XLII.

Fraction.	Per cent.	Weight.	Cut C or C_2-C_1	Change of Density. 90 per cent.	81 per cent.	Actual.	Density Actual.	Atomic Weight.
1	25	650	1.33	−24.7	−22.2	−22.2	−44.4	−0.0089
2	25	650	2 −1.33	−14.8	−13.3			
3	25	650	4 −2	0	0			
4	25	650	4	+39.5	+39.5			

In each of the two above tables the column headed "Change of Density, 90 per cent.," *gives the theoretical values for the separation based upon the separation coefficient .0057, which is the highest separation so far obtained in any evaporation at low pressures.* The reason for calling this a 90 per cent. value is that, as stated before, Mulliken has obtained a separation by diffusion through filter paper which is represented by the coefficient 0.0063. Runs VI to VIII were simply repetitions of that listed in Table XLIII. Run IX gave 55 c.c. with $\Delta = -65.2$, where Δ is the increase in density in parts per million.

Runs X to XII were made on the basis of a 50 per cent. cut. Here the increase and decrease of density should both be 17.7 parts. In the tenth run the 55 c.c. from run IX was split in this way and the theory indicated that the density should be $\Delta = -(65.2 + 17) = 82.2$. In the eleventh run this was divided in the same way again, with an estimated $\Delta = -(82.2 + 17.7) = 99.9$, and in the twelfth, $\Delta = -(99.9 + 15.9) = 115.8$. The determined value was $\Delta = -112.4$, which indicates that the efficiency was high. It should be said that the calculations of this paragraph were made on the basis of 0.0057 as the highest experi-

mental separation coefficient for a vaporization process. The seventh fraction of runs I to V (Table XLII) were combined, which gave 50 c.c. with an estimated Δ of +36. This was evaporated into three nearly equal fractions. The last fraction of 17 c.c. was combined with the eighth fractions of runs II to V. This gave 65 c.c. with an estimated Δ of +64, which was evaporated down to 12 c.c. with an estimated $\Delta = +106.5$, and a determined value of 95.9. This indicates that the last evaporations were less efficient than the others.

The total difference of density obtained in about twenty days of operation of this apparatus was 266 parts per million, or an atomic weight difference of 0.053. The end fractions are quite large, however, and weigh 224 grams for the light, and 272 grams for the heavy fraction. The difference of atomic weight thus far secured is 0.070 unit and a few days of further operation will give a change equal to 0.110 unit.

71. SEPARATION OF THE ISOTOPES OF MERCURY BY DISTILLATION AT LOW PRESSURES.

The interesting fact that even in the ordinary purification of mercury by distillation at low pressures there is an easily measurable separation of the isotopes of mercury, commonly 4 to 7 parts per million increase of density of the residue, was first observed by Mulliken and Harkins.[93] A detailed study of such distillations by Mulliken showed that when the distillation flask has a neck of large diameter the efficiency of such a process may be made as great as 67 per cent. of that given by a completely irreversible evaporation, provided the water condenser is put as close to the flask as is possible; and Laby and Mepham [94] report a result which corresponds to an efficiency of 49 per cent. The most striking results of the investigation in this laboratory [95] are:

(1) Distillation at the rate of 15 c.c., or 204 grams per hour (3.5 gms./cm.^{2} hr.), from a 300-c.c. flask with a neck bent over and sealed to a water-jacketed condenser, gave an efficiency of 50 per cent., even when the air pressure was as 0.1 or 0.2 mm. Since the highest efficiency obtained by the evaporation method is only 90 per cent., it is seen that the extremely simple distillation method is a very good one. The efficiencies obtained at different

[93] Mulliken and Harkins: *J. Am. Chem. Soc.*, **44**, 60–62 (Jan., 1922).
[94] Laby and Mepham: *Nature*, **109**, 206 (1922).
[95] Mulliken: *J. Am. Chem. Soc.* (Nov., 1922).

pressures are: 58 per cent. at 10^{-5} mm., 54 per cent. at 0.02 mm., 46 per cent. at 0.8 mm., 20 per cent. at 10 mm., and 9 per cent. at 30 mm.

(2) *A film of material such as soot on the surface of the mercury increases the efficiency* of the separation markedly at moderate or high, but not at low, rates of vaporization. The following examples illustrate the considerable magnitude of this effect, the evaporation rates being given in grams per cm.^{2} per hour: (1) without film, efficiency 54 per cent. at 1.5 grams, 27 per cent. at 8 grams, and 24 per cent. at 24 grams; (2) with film, 58 per cent. at 3 grams, 49 per cent. at 14 grams, and 37 per cent. at 36 grams.

72. SEPARATION OF THE ISOTOPES OF MERCURY BY THE HIGHLY EFFICIENT AND RAPID METHOD OF EVAPORATIVE-DIFFUSION.

The combination method of evaporative-diffusion, as applied by Mulliken in this laboratory, is by far the most efficient of all of the processes as yet devised for the separation of isotopes. It also has the further great advantages that it requires only tap water for cooling, and that its efficiency is very high at air pressures as great as 0.2 mm., which means that the apparatus operates well with an oil vacuum pump of small size even when the pump is not in specially good order. The apparatus is by far the most rapid in its operation of any thus far tested; also more rapid than any yet devised, with the possible exception of a very large steel apparatus designed by the writer, but not constructed on account of its high cost.

Whereas the highest efficiency obtained by Broensted and Hevesy, or Mulliken and Harkins, by the use of a single evaporation, is 90 per cent. in terms of Mulliken's value of the separation coefficient, 0.0063, the evaporative-diffusion gives efficiencies as high as 120 per cent., and at very high speeds of operation the efficiency is 100 per cent., of which 25 per cent. is contributed by the evaporation, and the rest by the diffusion through filter paper. It can be easily seen that this indicates that the efficiency of the diffusion is *more* than 75 per cent., though this is not apparent without a careful consideration of the factors involved. A battery of six units has been constructed. Each unit consists of a 500-c.c. flask of pyrex glass, fitted with a long vertical tube of filter paper above it, the latter being surrounded by two concentric tubes of pyrex glass. Between these the water used for condensing is

passed. *By the use of the six units mercury can be evaporated with good efficiency at the rate of a ton in twenty-four hours or less.*

With only about four days of operation the three units first constructed gave 20 c.c. of mercury whose atomic weight is 0.030 unit higher, and 150 c.c. 0.016 unit lower than ordinary mercury, a total difference of 0.046 unit. At present 136 c.c. of −121 p.p.m. and 47 c.c. of +203 p.p.m. have been secured, with an atomic weight difference of 0.061 unit. It is obvious that the size of the fractions as well as the atomic weight change should be considered in connection with the degree of separation. If operated at about the present rate of diffusion, 680 grams of mercury vapor per hour per unit at 100 per cent. efficiency, the six units of this apparatus will give a full set of fractions of 680 grams each at intervals of 22 parts per million of density difference (0.0044 unit of atomic weight) with separations between the end fractions as follows: 0.1 unit of atomic weight difference in 86 hours, 0.2 unit in 717 hours, 0.3 unit in 2281 hours, etc. Thus in 228 days of 10 hours each, 47 kilos of mercury could be distributed evenly over a range of 0.3 unit of atomic weight, in the form of 69 fractions of 680 grams of mercury each. It is evident that a considerably greater atomic weight difference could be obtained in the same time by decreasing the size of the fractions.

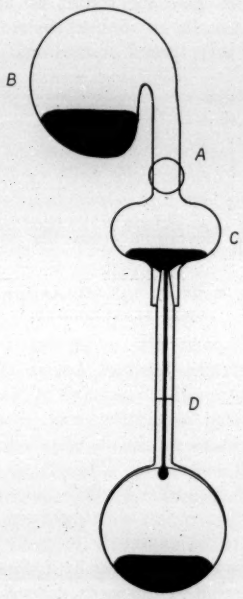
73. DETERMINATION OF THE DENSITY OF MERCURY.

The density of mercury is determined by the use of a special pycnometer,[84] by means of which it is probable that a precision of one part in 5 million can be attained. With very ordinary precautions the variation is about 1 part in 2 million. The pycnometer consists of a glass bulb sealed to a capillary of 0.2 mm. internal diameter (Fig. 35D). This is fitted to a filling device (*BC*) by means of a tight ground-glass joint. The mercury is first poured into the bulb *B*, the empty pycnometer fitted in place, and the apparatus evacuated through the side tube *A* by means of a good oil vacuum pump. The device is then rotated around *A* until it is in such a position that the pycnometer becomes filled. The latter is then detached and put in a bath whose temperature is slightly above 25°, and by an amount which will cause the mercury meniscus to stand almost exactly on the

fine graduation on the stem, when the temperature is reduced exactly to 25.000°. The bulb *C* should contain more mercury than will fill the bulb of the pycnometer, in order to prevent any floating scum from entering the latter.

The edges of the tip of the pycnometer should be well rounded off. What is more important is that the inside of the

FIG. 35.



Pycnometer.

bulb shall be *very smooth*, with no projections of any kind, and also very clean when it is first made. The capillary should have a uniform diameter, but if it is to be used in warm weather, a small bulb may be blown in it near the top, in order to prevent an overflow by expansion during the period of weighing.

Corrections for the buoyancy of the air with varying humidity and barometric pressure may be avoided by the well-known

method of using an exactly similar pycnometer filled with mercury, but with a sealed capillary as a counterpoise. In routine work, however, it has been the custom to rest the single pycnometer in a cup of glass, whose weight has been so chosen that it exactly corrects for buoyancy changes. The former method has the advantage of giving a better correction for the weight of the film of moisture deposited on the outer surface of the glass. The following figures give the results of *five different fillings with two different samples as obtained in ordinary routine work* carried out without very special precautions:

	Filling.	Corrected weight of filled pycnometer.
Sample 1.	1	124.09393
	2	124.09398
Sample 2.	1	124.09391
	2	124.09400
	3	124.09397

Here the *maximum* deviation from the mean is 5 parts in 10 million.

74. EXPERIMENTAL WORK ON THE SEPARATION OF ISOTOPES BY LIQUID CENTRIFUGING.

Joly and Poole [96] were able to separate certain liquid alloys into fractions of different densities, but an attempt to apply this method to the separation of the isotopes of lead was unsuccessful. However, the expected separation was of the same order of magnitude as the errors in the density determinations, so the negative result is not surprising. The peripheral velocity in these experiments was 10^4 cm./sec. Poole [97] later discussed the possibility of securing a separation with mercury, but concluded that the density change to be expected, 30 parts per million, would be too small to be measured. Actually 1/60 of this density difference could be detected by the method developed in this laboratory, so Mulliken experimented with mercury in a large centrifuge, which, unfortunately, does not have a very high peripheral velocity. A speed of 2300 r.p.m. was attained, with the outer end of the steel tubes which contained the mercury 26.3, and the inner end 7.1 cm. from the axis. Each of the two tubes contained 13 c.c. The calculated separation between the extreme

[96] Joly and Poole: *Phil. Mag.* (6), **39**, 372 (1920).
[97] Poole: *Phil. Mag.* (6), **41**, 818 (1921).

ends is 8.8 parts per million, but, since the contents were divided into thirds, only two-thirds of this difference should be obtained, or 5.9 p.p.m. The results were conclusively negative to 0.5 part per million in each of two eight-hour runs. The tubes were as perfectly balanced as was possible, but in spite of this there was some vibration at the highest speeds of the centrifuge. It was not difficult to prove that this vibration is a sufficient cause of the failure of the separation, as is evidenced by the fact that when the mercury in the bottom half of the tube was made 12 parts per million heavier than that in the top half, a half-hour run was sufficient to mix the two halves thoroughly *against the effect of the centrifugal force.* That an eight-hour run should be sufficient to give a centrifugal separation if the vibration could be prevented, seemed to be indicated by the fact that when the two halves of the tube were filled with material differing in density by 12 p.p.m. as described above, and the tube was kept still on a concrete pier, the rate of diffusion was sufficiently great to very nearly eliminate the difference of density in eight hours of standing.

Mr. Jenkins and the writer will repeat the attempt to obtain a centrifugal separation. The tubes will be first filled with tightly packed steel balls, or possibly sand, the top screwed on tightly, and the mercury run in through a hole in the top. It is hoped that the presence of the small balls may sufficiently annul the vibration of the liquid to enable the detection of a separation, though it is not improbable that success will not be attained until a centrifuge with a higher speed and a lesser vibration can be obtained. It is probable that a special centrifuge must be constructed if any considerable separation is desired. If speeds of 10^5 cm. per second could be obtained without sufficient vibration to affect the result, a separation of 0.48 of a unit of atomic weight could be attained in one operation.

The values of the centrifugal separation coefficients (values for P in equation 28, section 68) have been calculated by Mulliken with the following results (times 10^{-12} at 20°): Li, 1.16; B, 1.85; Ne, 7.38; Mg, 8.97; Cl, 14.5; Ni, 18.4; Zn, 53; Br, 20.4, and Hg, 47. For ordinary *air* the coefficient would be about 62×10^{-12}. It will be noted that the coefficients are very favorable to the heavy elements, and this should be particularly true of the elements of even atomic numbers between 30 and

80. A peculiarity of these coefficients, as compared with diffusion coefficients, is that the former are independent of the state of combination of the element, and are thus characteristic of the element, while the latter are inversely proportional to the molecular weight.

75. THEORY OF THE SEPARATION OF ISOTOPES BY NON-EQUILIBRIUM EVAPORATION.[98]

The surface of a liquid may act as a diffusion membrane in which the aperatures are of molecular dimensions. Since this represents the simplest type of diffusion membrane the equations for the separation of isotopes by diffusion will be developed from a consideration of this special case. Meyer has shown in a very simple way [99] that the number (N) of molecules of a gas at rest which strike 1 square centimetre of the wall of the containing vessel, is given by the following equation:

$$N = \frac{1}{4} nv \qquad (A)$$

in which n is the number of molecules in 1 cubic centimetre of the gas, and v is the *average* velocity of its molecules.

According to the Maxwell distribution law the probability (y) of a velocity whose magnitude is x is given by the equation

$$y = \frac{4}{\sqrt{\pi}} x^2 e^{-x^2} \qquad (B)$$

From this equation it may be seen that the relation between the average velocity and the mean velocity (c) is

$$v = c\left(\frac{8}{3\pi}\right)^{1/2} \qquad (C)$$

so equation (A) becomes

$$N = \frac{1}{4} nc\left(\frac{8}{3\pi}\right)^{1/2} = \frac{1}{\sqrt{6\pi}} n.c \qquad (A')$$

The kinetic energy of translation of one mol of gas molecules is given by the well-known equation:

$$E = \frac{1}{2} M c^2 = \frac{3}{2} RT \qquad (D)$$

so

$$c = \sqrt{\frac{3RT}{M}} \qquad (E)$$

[98] This and the following sections on the theory of the separation of isotopes have been taken largely from a paper by Mulliken and Harkins, *J. Am. Chem. Soc.*, **44**, 37–65 (1922).

[99] Meyer: "Kinetic Theory of Gases" (1899), pages 80 to 83.

A combination of equations (A) and (E) gives

$$N = n\left(\frac{RT}{2\pi M}\right)^{1/2} \qquad (F)$$

Now $nM = \rho$, where ρ is the density of the gas, and is given by the equation

$$\rho = \frac{M}{V} = \frac{MP}{RT} \qquad (G)$$

in which M is the molecular weight and V is the molecular volume. So

$$n = \frac{P}{RT} \qquad (H)$$

A combination of (F) and (H) gives our fundamental equation

$$N = \frac{P}{\sqrt{2\pi MRT}} \qquad (I)$$

Equation (1) gives the number of molecules of a dilute vapor which strike one square centimetre of the surface of a pure liquid in equilibrium with it, and so necessarily the number which evaporate from unit area in unit time. For an ideal solution, such as a mixture of isotopes, the relation $N_a = \frac{px_a}{\sqrt{2\pi MRT}}$ should hold for each isotopic component (a), if the vapor pressure has the same value (p) for each such component when pure. That this is at least very closely true is shown by Aston's failure to obtain any separation of the isotopes of neon by 3000 fractionations, and by other evidence.[100] In an ordinary distillation, the rate of distillation is negligibly small compared with N, and there is practical equilibrium between liquid and vapor. Although lighter molecules evaporate faster from the liquid, they also return faster from the vapor, so that the two phases have practically the same isotopic composition. If, however, the pressure is made very low, and the condensing surface placed so close to the evaporating surface that practically all the evaporating molecules are condensed, it is clear that the condensate must be enriched in the lighter isotopes. This method of evaporation is really equivalent to molecular effusion.

[100] In view of the thermodynamic relation between vapor pressure and solubility, the failure of Richards and Hall [*J. Am. Chem. Soc.*, **39**, 531 (1917)], to secure any change of atomic weight by 1000 recrystallizations of lead nitrate from radioactive material, is additional evidence for the very close equality of the vapor pressures of isotopes.

The molecules leaving a liquid surface move forward with various velocities and in various directions. The farther a molecule has to travel before reaching a cold surface, the greater is its chance of collision with another molecule; and the greater the number of collisions it suffers, the more likely it is to acquire a backward component of velocity. If there are many collisions per molecule, the condition of a saturated vapor is approached, and the efficiency of the separation is reduced. The presence of air-molecules, which, being non-condensable, and moving in all directions, will increase the number of unfavorable collisions. For maximum efficiency, (1) the apparatus must be thoroughly evacuated, (2) the rate of evaporation must be sufficiently low, and (3) the condensing surface must be as close as possible to the evaporating surface. At least in the case of mercury (which has very heavy atoms), as shown by the present experimental work, the atoms can move through a distance equal to several times the mean free path for the saturated vapor, and can suffer a number of collisions, without much loss of efficiency.

In order that the theoretical efficiency shall be attained, the evaporating liquid must be kept at a uniform composition throughout, by diffusion, convection, or by artificial mixing. Otherwise the accumulation of heavy molecules in the surface will cause a corresponding increase in their proportion in the condensate. Approximate calculations indicate, however, that liquid diffusion alone is capable of preventing more than a slight loss of efficiency, even for fairly considerable rates of evaporation. This is in harmony with the experimental results. Because of the impossibility of rapid mixing, the separation of isotopes by evaporation from a solid surface is evidently impracticable. The range of application of the method may, however, be extended by the use of solvents.

Comparison of Methods.—The choice of elements suitable for separation by evaporation is limited to those forming suitable compounds or solutions or themselves existing as liquids having a small vapor pressure at a convenient temperature. To be suitable for a diffusion method, a substance must exist as a gas or have a considerable vapor pressure preferably at room temperature. The diffusion method probably has wider applicability than the evaporation method.

76. DEVELOPMENT OF EQUATIONS SHOWING RATE OF CHANGE OF COMPOSITION AND ATOMIC WEIGHT IN DIFFUSION PROCESSES.

Notation.

(Letters preceded by a (*) in the following list are always used with one of the subscripts 1, 2,—*a*—*b*—*s*—*n*, each of which is used to refer to a particular molecular species; *a* and *b* refer to *any* molecular species, *s* and *n* to the last of a set or series. Letters preceded by a (+) may be used with the subscript ₀ to denote initial values of the quantities to which they refer, for example, N_0, $(N_1)_0$ $(x_a)_0$.

$(*)N$	= rate of flow in mols per sec.
$(+)N$	= total number of mols of material in *residue* at any time during a diffusion
$(*+)N$	= number of mols of an individual component in the *residue*
$(*+)x$	= mol-fraction
$(*)x$	= increase in mol-fraction of a component over its initial value, in the residue; $(*)\Delta^c x$, in the *total condensate;* $(*)\Delta^{ic}x$, in the instantaneous condensate
M	= ordinary (average) molecular weight
$(*)M$	= molecular weight of a particular isotope
	ΔM, $\Delta^c M$, $\Delta^{ic}M$, increase in molecular weight of residue, total condensate, and instantaneous condensate, respectively
k^1_a	$= \sqrt[c]{M_1/M_a}$, where c is between 2 and 1; for example $k^1_3 = \sqrt[c]{M_1/M_3}$
k^1_1	$= \sqrt[c]{M_1/M_1} = 1$
R	= gas constant
T	= absolute temperature
$(*)p$	= saturated vapor pressure (or, gaseous pressure in general)
r	= radius of capillary tube; l = length of same
$(*)\lambda$	= mean free path of gas molecules
$(*)c$	= mean velocity of gas molecules
$(*)n$	= number of mols, or molecules, per c.c.
$(*)\frac{\delta n}{\delta z}$	= concentration gradient
$(*)d_1s$, d_2s, etc.	= distance between centres of molecules 1 and *s*, or 2 and *s*, respectively, at impact; for example d_{12}, d_{21}. Note that d_{11} or d_{12} become d_1 and d_2
A, A', B, B'	= (see Equations 5, 5′, 7 and 7′)
$C = N_0/N$	= "cut"
D, D', E, E'	= (see Equations 6A, 6A′, 7A, 7A′)
S	$= \Sigma(x_a k^1_a) = x_1 + x_2 k^1_2 + \ldots x_n k^1_n$
n_e	= number of atoms of an isotopic element in a compound, *e.g.*, for CCl_4, $n_e = 4$

Change in Composition of Residue for the Case of Two Isotopes.—For a mixture of two isotopes having molecular

weights M_1 and M_2, and mol-fractions x_1 and x_2, the relative rate of molecular diffusion, molecular effusion, or evaporation, is given by

$$-dN_2/-dN_1 = (x_2/\sqrt{M_2})\ (\sqrt{M_1}/x_1) = (x_2/x_1)\ \sqrt{M_1/M_2} = k_2^1\ (x_2/x_1). \quad (1)$$

N_1 and N_2 denote the respective numbers of mols of the two isotopes in the *residue* at any time. N will be used to denote $N_1 + N_2$, and N_o to denote the number of mols initially present. For gaseous diffusion, the relation is the same, except that k_2^1 means $c\sqrt{M_1/M_2}$, where c is some number between 1 and 2. Rearranging Equation 1 and noting that $N_1 = N.x_1$ and $N_2 = N.x_2$

$$dN_2/x_2 = k_2^1 dN_1/x_1 \text{ or } \frac{N dx_2 + x_2 dN}{x_2} = k_2^1\left(\frac{N dx_1 + x_1 dN}{x_1}\right).$$

$$\text{Then,} \quad (1-k)\ dN/N = k\left(\frac{dx_1}{x_1}\right) - \frac{dx_2}{x_2}. \quad (2)$$

Integrating,

$$(1-k)\ ln\ N/N_o = k\ ln\ (x_1/(x_1)_o) - ln(x_2/(x_2)_o).$$

Or, denoting N_0/N, the "cut," by C,

$$(1-k)\ \log C = k\ (\log(x_1)_o - \log x_1) - \log (x_2)_o + \log x_2. \quad (3)$$

This equation can be used to calculate the cut necessary to obtain any desired change in the composition of the residue, the initial composition being known. The change in atomic weight of the residue for a given change in composition may be obtained from the relation, $\Delta M = (M_2 - M_1)\Delta x_2$.[101] For the diffusate, the change, $\Delta' M$, is exactly $-\Delta M/(C-1)$ (see Equation 14, p. 90). In connection with his work on the separation of the rare gases, Rayleigh[102] developed a less direct but simpler equation, which is rather more convenient for calculation than Equation 3. He uses the term enrichment ratio, symbolized by r, for $\frac{x_2/(x_2)_o}{x_1/(x_1)_o}$. Using the symbols of the present section, Rayleigh's relation can be reduced[103] to

$$C = [x_1/(x_1)_o] \cdot r^{1/1-k} \quad (4)$$

[101] In general, for a mixture of (n) isotopes, if the atomic or molecular volumes are equal, as the work of Richards and Wadsworth [*J. Am. Chem. Soc.*, **38**, 221 (1916)] shows to be true in the case of the atomic volume of solid lead, $\Delta M = (M_2 - M_1)\Delta x_2 + (M_3 - M_1)\Delta x_3 + \ldots (M_n - M_1)\Delta x_n = \Sigma(M_a - M_1)\Delta x_a$. This relation applies to mixtures of isotopic atoms or of isotopic molecules, *i. e.*, molecules differing only in containing atoms which are isotopes of each other, *e.g.*, HCl_{35} and HCl_{37}; $CH_2(Cl_{35})_2$, $CH_2Cl_{35}Cl_{37}$, and $CH_2(Cl_{37})_2$; $Mg_{24}O$, $Mg_{25}O$, and $Mg_{26}O$.

[102] Rayleigh: *Phil. Mag.*, [5] **42**, 493 (1896).

[103] See Sections 65 and 66.

This is readily obtained from (3). If r is near unity, Equation 4 becomes, very nearly, $C = r^{1/1-k}$. In making calculations of C in terms of ΔM or Δx, the easiest method is to calculate $1/(1-k)$ (compare Table XLI) once for all for the compound under consideration, then to calculate the value of r corresponding to the assumed value of ΔM or Δx, and finally to apply Equation 4. $\Delta' M$, the decrease of atomic weight for the *diffusate*, equals $-\frac{\Delta M}{C-1}$.

Simple Equations for Change of Composition of Residue for Small Cuts.—The use of the exact relations (3) and (4) involves much calculation. For small cuts, or approximate calculations with larger cuts, a very simple relation, which shows clearly the factors governing the rate of separation, can be derived from Equation 2. Noting that $dx_1 = -dx_2$, Equation 2 becomes $(1-k)\,dN/N = (-k/x_1)\,dx_2 - dx_2/x_2$. Noting that $-dN/N = -\frac{d(N/N_0)}{N/N_0} = d \ln C$, this reduces to

$$dx_2 = -dx_1 = \frac{(1-k)x_1x_2}{x_1+kx_2}\, d\ln C = A\, d\ln C. \qquad (5)$$

This quantity A is really the slope, at the point $(x_2, \ln C)$, of the curve obtained by plotting x_2 (or $-x_1$) against $\ln C$, starting with $C = 1$ for $x_1 = (x_1)_0$ and $x_2 = (x_2)_0$. As the composition changes only very slowly with the cut, A is nearly a constant, so that

$$\Delta x_2 = \frac{(1-k)\,x_1x_2}{x_1+kx_2}\cdot \ln C, \text{ nearly.} \qquad (6)$$

By taking average values of x_1 and x_2 this equation will hold rather closely even for a large cut. For the change in atomic weight of the residue,

$$\Delta M = (M_2 - M_1)\Delta x_2 = \frac{(1-k)x_1x_2(M_2-M_1)}{x_1+kx_2}\cdot \ln C = B \ln C. \qquad (7)$$

Note that C is strictly a ratio of mols, or of volumes. Unless C is extremely large, however, it may without much error be considered a ratio of masses. From Equations 6 and 7 it is seen that the increase in the mol-fraction of heavy isotope and in the atomic weight of the residue proceed arithmetically as the quantity of the latter diminishes exponentially.

Relation of Rate of Separation to Composition of an Isotopic Mixture.—The rate at which A and B *change* with the composition or atomic weight of the residue during a diffusion or evapora-

tion can be obtained to a close approximation as follows. Since $x_1 + kx_2$ is always nearly unity, we can write

$$A = \left(\frac{1-k}{x_1+kx_2}\right). \; x_1x_2 = Fx_1x_2, \text{ and } B = \frac{1-k}{x_1+kx_2}\,(M_2-M_1)x_1x_2 = Gx_1x_2,$$

F and G being regarded as essentially constant. Then

$$\frac{dA}{dx_2}\left(=\frac{dB}{dM}\right) = F\,\frac{d(x_1x_2)}{dx_2} = F\,\frac{d(x_2-x_2^2)}{dx_2} = F(1-2x_2) = F(x_1-x_2) = \frac{A(x_1-x_2)}{x_1x_2}. \quad (8)$$

If values of A or B are plotted as ordinates against values of x_2 (or $-x_1$) as abscissas, *a portion of a parabola is obtained,* corresponding to the equation $A = Fx_1x_2 = F(x_2 - x_2^2)$, or $B = G(x_2 - x_2^2)$. This begins at the point ($x_2 = 0$, A or $B = 0$), rises to a maximum at ($x_2 = 0.50$, $A = 0.25F$ or $B = 0.25G$), and falls again to ($x_2 = 1$, A or $B = 0$). Thus *the most favorable mixture for the separation of two given isotopes is that for which* $x_1 = x_2 = 0.50$. Between $x_2 = 0.25$ and $x_2 = 0.75$ the value of B is still nearly as favorable, but if x_2 falls below 0.05 or 0.10, or rises above 0.90 or 0.95, the rate of separation is much reduced. If x_2 (or M) is plotted against ln C for the residue, the slope A (or B) of this curve thus approaches zero, and *the curve itself approaches asymptotically the line* $x_2 = 1$ (or $M = M_2$), as ln C continues to increase;[104] the curve is terminated abruptly in the other direction at $C = 1$.

The slope dA/dx_2 of the A parabola is given by Equation 8. Since $B = (M_2 - M_1)\,A$, and $\Delta M = (M_2 - M_1)\Delta x_2$, it is evident that dB/dM is equal to dA/dx_2. From Equation 8, then, dB/dM is zero when $x_2 = 0.50$, has a maximum positive value when $x_2 = 0$, and a maximum negative value when $x_2 = 1$. Thus B (and A) increase for the residue (and decrease for the diffusate), during a separation, if x_2 is less than x_1; and *vice versa.*

Modifications of Simple Equations for Large Cuts.—The quantity $\frac{dB/B}{dM}$ is useful as a measure of the error in B when ΔM is large.

$$\frac{dB/B}{dM} = \frac{F(x_1-x_2)}{B} = \frac{x_1-x_2}{x_1x_2(M_2-M_1)}.$$

Call this last quantity $2H$. For a moderately large change ΔM of atomic weight we have, approximately,

[104] See Fig. 36, particularly the curve for lithium.

$$\Delta M = \left[B + \tfrac{1}{2}\left(\frac{\mathrm{d}B}{\mathrm{d}M}\right)\Delta M\right] \ln C = B\left[1 + \tfrac{1}{2}\left(\frac{\mathrm{d}B/B}{\mathrm{d}M}\right)\Delta M\right] \ln C =$$

$$B\,(1 + H.\Delta M)\ln C. \qquad (9)\ ^{105}$$

For the case that $M_2 - M_1 = 2$, if $x_2 = 0.01$, the value of H is 24.8; if $x_2 = 0.10$, $H = 2.22$; if $x_2 = 0.25$, $H = 0.67$; if $x_2 = 0.50$, $H = 0$; if $x_2 = 0.75$, $H = -0.67$, etc. The correction term $H\Delta M$ is evidently not large unless ΔM is considerable, or x_2 is near zero or unity. For ordinary hydrogen chloride, $x_2 = 0.23$, $B = 0.00950$, and $H = +0.76$. Without using the correction term, we have, for $\Delta M = 0.05$, $\Delta M = 0.05 = 0.00950 \ln C$. By putting in the correction term, $\Delta M = 0.05 = 0.00950\ (1.038) \ln C$. The value of C calculated from the former expression (Equation 7) is 192.7; that from the latter (Equation 9) is 158.9. The *correct* value of C, calculated by means of Equation 4, is 159.8. For $\Delta M = 0.10$, the respective values of C obtained by the three methods are 37,140; 17,630; and 18,530. The discrepancies between the results of Equation 4 and Equation 7 are not large, especially from the point of view of the change of atomic weight secured by a given cut, and are in fact much less than would normally result between theory and practice due to unavoidable inefficiency of operation. Equation 9 evidently gives a very close approximation of the results of the exact Equation 4, and is much simpler than the latter, once the values of B and H have been calculated for the compound under consideration. Values of B are given in Table XLI. Equation 10, which likewise gives a very close approximation, is useful for calculating ΔM if C is given.

Useful Approximate Forms of Simple Equations; Relation of Rate of Separation to Molecular Weights of Isotopes.—The term $(1 - k)$ in Equations 6 and 7 can be calculated very quickly and accurately by means of the approximate empirical relation $(1 - k) = (4/c)\ (M_2 - M_1)/(3M_2 + M_1)$. This is correct to within about 0.1 per cent. for the lightest elements, and is *still more exact* for the heavier elements. For example, the exact value of $1 - k$, for $c = 2$, and $M_1 = 6$ and $M_2 = 7$, is 0.074180, while that calculated from the above relation is 0.074074, or 0.14 per cent. too low. For $M_1 = 36$, $M_2 = 38$, the exact value of $1 - k$ is 0.026672, and the approximate value 0.026667; the latter is only 0.018 per cent. low. Using the relation just given, Equation 6 becomes

[105] Since $\Delta M = B \ln C$, nearly, this can also be written,

$$\Delta M = B(1 + BH \ln C) \ln C. \qquad (10)$$

$$\triangle x_2 = \frac{(M_2 - M_1)x_1x_2}{(c/4)(3M_2 + M_1)(1-(1-k)x_2)} .ln\ C = A\ ln\ C \text{ (practically).} \qquad (6B)$$

and Equation 7 becomes

$$\triangle M = \frac{(M_2 - M_1)^2x_1x_2}{(c/4)(3M_2 + M_1)(1-(1-k)x_2)} .ln\ C = B\ ln\ C \text{ (practically).} \qquad (7B)$$

A and B can be calculated with sufficient accuracy in accordance with these equations, the term $(1-(1-k).x_2)$ being readily calculated by the help of the relation given. This term can be neglected entirely for neon and heavier elements, when an accuracy of 1 per cent. is sufficient, giving simplified forms of Equations 6B and 7B which may be called Equations 6BB and 7BB. These can be still further simplified to [106] the still less exact forms,

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[106] $(1-k) = 1 - \sqrt[c]{M_1/M_2} = 1 - \sqrt[c]{1-(M_2-M_1)/M_2} = 1 - \sqrt[c]{1-c(M_2-M_1)/cM_2} = 1 - \sqrt[c]{[1-(M_2-M_1)/cM_2]^c}$ (nearly) $= 1 - [1-(M_2-M_1)/cM_2]$, (nearly) $= (M_2-M_1)/cM_2$, (nearly). The usual case is $c = 2$, but the relation holds for any value of c (it is of course exact for $c = 1$), provided $M_2 - M_1$ is small compared with M_2. The empirical relation $(1-k) = (4/c)\ (M_2-M_1)/(3M_2+M_1)$ holds very closely even when $M_2 - M_1$ approaches M_2 in magnitude. This relation reduces to $2(M_2-M_1)/(3M_2+M_1)$ for $c = 2$. This can be used for calculating B of Equation 7.

The quantity $(1-k)$ is closely related to the "diffusion exponents" (k) and (k') of Harkins and Hayes. (k) is equal to $-1/(1-k)$, and (k') to $-1/(1-(1/k)) = +k/(1-k)$. The "diffusion exponent" is the same (except for the sign) as the exponent of r in Equation 4 of this section. The rule of Harkins and Hayes that $\frac{(k)+(k')}{2} = (M_1+M_2)/(M_1-M_2)$, (k) and (k') being respectively 0.50 unit greater, or less, than $(M_1+M_2)/(M_1-M_2)$, agrees with the above empirical relation for $1-k$. [The relation $(k)-(k') = 1$ is an exact and necessary one, for $(k) = {}^c\sqrt{M_1}/({}^c\sqrt{M_1} - {}^c\sqrt{M_2})$, and $(k') = \sqrt[c]{M_2}/(\sqrt[c]{M_1} - \sqrt[c]{M_2})$]. The approximations $(1-k) = (M_2-M_1)/cM_2$[1], and the analogous $(1-1/k) = (M_1-M_2)/cM_1$ [2], are less exact then the approximations $(1-k) = (4/c)\ (M_2-M_1)/(3M_2+M_1)$ [3], and $(1-1/k) = (4/c)\ (M_1-M_2)/(3M_1+M_2)$ [4]. For, using [1] and [2], while $\frac{(k)+(k')}{2} = (-\frac{1}{2})[(1/1-k)+1/(1-(1/k))] = \frac{M_1+M_2}{M_1-M_2}$, comes out as it should, the result $(k)-(k') = 2$ is obviously wrong. Using Equations [3] and [4] for $(1-k)$ and $(1-(1/k))$, $(k)+(k') = (M_1+M_2)/(M_1-M_2)$, and $(k)-(k') = 1$, as it should. The relation of Equation 3, and the corresponding relations, $(k) = (3M_2+M_1)c/4(M_1-M_2)$, and $(k') = (3M_1+M_2)c/4(M_1-M_2)$, prove to be so nearly exact that they can be used for calculations by the exact Equation 4.

$$\triangle x_2 = [(M_2 - M_1)x_1x_2/cM_2]ln\ C = D\ ln\ C \qquad (6A)$$

and

$$\triangle M = [(M_2 - M_1)^2x_1x_2/cM_2]\ ln\ C = E\ ln\ C \qquad (7A)$$

This form of Equation 7 brings out the dependence of the "*separation coefficient*" B on the *total molecular weight* and on the *interval between the molecular weights* of the two isotopes. For calculations of the separation coefficient, Equation 7B is practically as exact as Equation 7; and Equation 7BB gives results which are very little in error, except for the lightest elements. The very simple approximation given by Equation 7A gives results at worst 3 per cent. low, for elements above neon, but in general Equation 7B or 7BB should be used.

Change of Composition for Diffusate.[107]—While the residue is being enriched in the heavier isotopes, the diffusate or condensate is being enriched in the lighter isotopes. For the "instantaneous" diffusate or condensate coming from material of a given composition (x_1, x_2) we can write

$$(x_1)^{ic}\frac{dN_1}{dN_1+dN_2} = \frac{x_1/c\sqrt{M_1}}{x_1/c\sqrt{M_1}+x_2/c\sqrt{M_2}}.$$

From this can be obtained [108] the *exact* equations

$$(\triangle^{ic}x_1)_{=} = \frac{(1-k)x_1x_2}{x_1+kx_2} = +A \qquad (11)$$

and

$$\triangle^{ic}M = -(\triangle^{ic}x_1)\ (M_2 - M_1) = \frac{(1-k)x_1x_2(M_2-M_1)}{x_1+kx_2} = -B \qquad (12)$$

The composition of the instantaneous diffusate or condensate always keeps pace with that of the residue, x_1^{ic}, being just A units ahead of x_1, and M^{ic} just B units behind M (see Fig. 30). The composition of the *total* diffusate is an average of a series of

[107] This is not given by the equations of Rayleigh.

[108]
$$\frac{x_1/c\sqrt{M_1}}{x_1/c\sqrt{M_1}+x_2/c\sqrt{M_2}} = \frac{x_1c\sqrt{M_2}}{x_1c\sqrt{M_2}+x_2c\sqrt{M_1}} = \frac{x_1}{x_1+k^1{}_2x_2}$$

Then

$$x_1^{ic}-x_1 = \triangle^{ic}x_1 = \frac{x_1}{x_1+kx_2} - x_1 = \frac{x_1-x_1^2-kx_1x_2}{x_1+kx_2} =$$
$$\frac{x_1-x_1^2-kx_1(1-x_1)}{x_1+kx_2} = \frac{(1-k)x_1x_2}{x_1+kx_2}$$

continuously changing instantaneous diffusates. It obviously approaches that of the original material as the *quantity* of residue approaches the vanishing point. For a mixture of two or any number of isotopes the mol-fraction x_a of *any* component (a) in the total diffusate is necessarily

$$x^c_a = \frac{(N_a)_o - N_a}{N_o - N} = \frac{(x_a)_o N_o - x_a N}{N_o - N} = \frac{(x_a)_o C - x_a}{C-1};$$

and

$$x^c_a - (x_a)_o = \triangle^c x_a = \frac{(x_a)_o C - x_a}{C-1} - (x_a)_o = \frac{(x_a)_o - x_a}{C-1} = \frac{-\triangle x_a}{C-1} \qquad (13)$$

where Δ^c, x^c_a, etc., refer to the diffusate, x_a, Δ, etc., to the residue. Correspondingly,

$$\triangle^c M = \Sigma(M_a - M_1)\,(\triangle^c x_a) = \frac{\Sigma(M_a - M_1)\,(-\triangle x_a)}{C-1} = \frac{-\triangle M}{C-1}. \qquad (14)$$

Equations 13 and 14 must hold independently of the nature or efficiency of the diffusion process, and depend only on the assumption that isotopes have equal atomic or molecular volume. By means of these relations, for a 100 per cent. efficient process, we have at once,

$$\triangle^c x_a = -A\,\frac{ln\ C}{C-1} \qquad (15)$$

and

$$\triangle^c M = -B\,\frac{ln\ C}{C-1}, \qquad (16)$$

and corresponding approximate relations with D and E. By putting $C = 1$ and noting that the limit of $ln\ C/(C-1)$ is unity, as C approaches unity, Equations 13 and 14 reduce to 11 and 12. For the result of n successive identical operations on the light fraction, equations analogous to 9 and 10 can be written, *viz.*,

$$\triangle^c M = -nB\,(1 + H\triangle^c M)\,ln\ C/(C-1), \qquad (17)$$

and

$$\triangle^c M = -nB\,[1 - BH\,ln\ C/(C-1)]\,ln\ C/(C-1), \qquad (18)$$

where C is the cut in *each operation.*

Effect of Back Pressure on Efficiency.—In molecular diffusion and molecular effusion, the fractional loss of efficiency due to back pressure is equal to the ratio of the back pressure to the initial pressure. This is shown by the following considerations. The *actual* increase, $\overline{\Delta x}$, in the mol-fraction of any isotope in the

diffusate, may be considered as the net result of two processes, forward and backward diffusion, which can be treated as independent (see earlier discussion). Letting Δx denote the increase for a 100 per cent. efficient process, and N_1 and N_2 the quantities of material which diffuse forward and backward, respectively, we can write with a slight approximation,

$$\overline{\Delta x} = \frac{N_1\overline{\Delta x} - N_2(\overline{\Delta x}+\Delta x)}{N_1 - N_2}.$$

Simplifying,

$$\overline{\Delta x} = \left(\frac{N_1 - N_2}{N_1}\right)\Delta x = \left(\frac{p_1 - p_2}{p_1}\right)\Delta x.$$

The efficiency of the process is $\overline{\Delta x}/\Delta x$, and is thus equal to $\frac{p_1 - p_2}{p_1}$; and the loss of efficiency is p_2/p_1. Analogous considerations apply to non-equilibrium evaporation, if p_1 and p_2 now stand for rate of evaporation and rate of return of molecules, respectively. With gaseous diffusion the case is more complicated, but analogous effects are to be expected.

77. GENERAL RELATIONS FOR ANY NUMBER OF ISOTOPES.

For the general case of a mixture of n isotopes, exact and approximate slope equations analogous to (5), (6), and (7) can be obtained in the following way. N separate equations of the form of Equation 1 can be written, *viz.*,

$$dN_a/x_a = k^1_a dN_1/x_1 \qquad (1')$$

and correspondingly, n equations of the form of Equation 2, *viz.*,

$$(1 - k^1_a)dN/N = k^1_a dx_1/x_1 - dx_a/x_a. \qquad (2')$$

The equation for which $a = 1$ is included for the sake of generality in the subsequent development. It is convenient to write all the equations in terms of the lightest component, (1), although any other component could have been chosen. From the a^{th} equation of the form of (2), one can get $dx_a = k^1_a(x_a/x_1)\,dx_1 - x_a(1 - k^1_a)dN/N$. Now it is evident that $dx = 0$. Then

$$\Sigma dx_a = \Sigma[k^1_a(x_a/x_1)dx_1 - (1 - k^1_a)x_a dN/N] = 0.$$

Or

$$(dN/N)\,\Sigma\,(x_a - x_a k^1_a) = (dx_1/x_1)\Sigma x_a k^1_a.$$

Or

$$(dN/N)\,(1 - \Sigma x_a k^1_{a'}) = (dx_1/x_1)\Sigma x_a k^1_a.$$

Denoting $\Sigma x_a k^1_a$ by S, this becomes $\frac{1-S}{S}\cdot\frac{dN}{N} = dx_1/x_1$. By sub-

stituting the value $dx_1/x_1 = (1/k^1_a)\ [(1 - k^1_a)\ dN/N + dx_a/x_a]$, obtained from equation $(2')$, and simplifying, the general expression for any isotope (a),

$$dx_a = \frac{x_a(k^1_a - S)}{S} \cdot dN/N = \frac{x_a(S - k^1_a)}{S} \cdot d\,ln\ C = A'_a\, d\,ln\ C, \qquad (5')$$

is obtained. This is the general form of the slope Equation 5, and can be treated like the latter. Thus

$$\triangle x_a = \frac{x_a(S - k^1_a)}{S}\ ln\ C, \text{ nearly.} \qquad (6')$$

Since $\Delta M = \Sigma[(M_a - M_1)\Delta x_a]$,

$$\triangle M = \frac{\Sigma[(M_a - M_1)x_a(S - k^1_a)]}{S} \cdot ln\ C = B'\ ln\ C, \text{ nearly.} \qquad (7')$$

This summation has n terms. It can be shown [109] that the following relation also holds approximately

$$\triangle M = \frac{\Sigma x_a x_b (M_a - M_b)^2}{c\,M} \cdot ln\ C = E'\ ln\ C \qquad (7A')$$

where a and b take independently every value from 1 to n, like terms, however, being taken only once. This summation has $\frac{n(n-1)}{2}$ different terms. *The calculation of E' is simpler than that of B' if n is not too large; and E'* usually *approximates B'*

[109] Since $1 = \Sigma x$, we can write $S - k^1_a = (x_1 k^1_1 + x_2 k^1_2 + \ldots + x_n k^1_n) - (x_1 + x_2 + \ldots + x_n) k^1_a = x_1(k^1_1 - k^1_a) + x_2(k^1_2 - k^1_a) + \ldots + x_n(k^1_n - k^1_a)$. In general $k^1_b - k^1_a = (1 - k^1_a) - (1 - k^1_b) = (M_a - M_1)/cM_a - (M_b - M_1)/cM_b$, nearly (see note on earlier page), $= (M_1/c)\ (M_a - M_b)/M_a M_b$. Applying this relation to the expression for $S - k^1_a$, the latter becomes $(M_1/c)\ (1/M_a)\ \Sigma[x_b(M_a - M_b)/M_b]$, where the subscript b, like a, stands for all numbers from 1 to n, to be chose, however, independently of the series of values for a. By application of this relation, Equation 5 can be written approximately, $dx_a = (x_a/c)\ \Sigma[x_b(M_a - M_b)\ M_b]$. d $ln\ C$ (5A'), since S is very nearly unity.

The summation in Equation $7'$ can be simplified as follows: $\Sigma(M_a - M_1) - x_a(S - k^1_a) = S\ \Sigma\ M_a x_a - \Sigma M_a x_a k^1_a - M_1 S \Sigma x_a + M_1 \Sigma x_a k^1_a = S\Sigma M_a x_a - \Sigma M_a x_a k^1_a - SM_1 + M_1 S = \Sigma\ (M_a x_a)\ (S - k^1_a)$. Equation $7'$ then becomes $\Delta M = \frac{ln\ C}{S} \Sigma (M_a x_a)\ (S - k^1_a)$. Applying the relation already obtained for $S - K^1_a$,

$$\Delta M = [M_1\ ln\ C)/cS].\ \Sigma([M_a x_a (1/M_a)]\Sigma\ [x_b(M_a - M_b)/M_b]).$$

This readily reduces to $\Delta M = (M_1/c)\ \frac{(ln\ C)}{S} \cdot \Sigma\ (x_a x_b (M_a - M_b)^2/M_a M_b)$. This gives the closely approximate relation

$$\triangle M = \frac{ln\ C}{cM} \cdot \Sigma\,[x_a x_b (M_a - M_b)^2] \cdot \qquad (7A')$$

very closely (see table of separation coefficients). The equations for the condensate are very easily generalized. Equations 11 and 12 become

$$\triangle^{ic}x_a = -A'_a \tag{11'}$$

and

$$\triangle^{ic}M = -B'. \tag{12'}$$

Equation 13 holds as it stands for any isotope a, and Equation 14 for the case of n isotopes; Equations 15 and 16 become

$$\triangle^{c}x_a = -A'_a \frac{ln\ C}{C-1} \tag{15'}$$

and

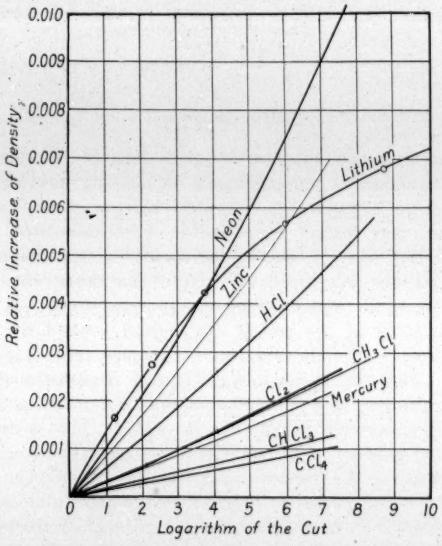
$$\triangle^{c}M = -B' \cdot \frac{ln\ C}{C-1}. \tag{16'}$$

Fig. 36 shows the increase of relative density for the residue or heavy fraction of various types of isotopic mixtures. The curves for neon, hydrogen chloride, chlorine, methyl chloride, chloroform, and carbon tetrachloride were calculated for the writer by Prof. A. C. Lunn, by the use of the approximate integrated equations developed by him. The other curves were obtained from the equations of the present paper. It will be noted that most of the curves are convex toward the X-axis, which indicates that the separation becomes more rapid as it proceeds. That this is not always true is demonstrated by the curve for lithium (that for boron is similar), which shows that the separation becomes rapidly less favorable. This is due to the fact that the product of the mol-fractions increases in a mixture of two isotopes as the composition *approaches* 50 per cent. of each component, and decreases as it recedes from this value, while the rate of separation varies directly as the product of the mol-fractions. In a mixture of two isotopes, if the ordinary atomic weight is less than the mean of the atomic weights of the isotopes, as is the case with neon, chlorine, potassium, and calcium, the separation of isotopes by means of the heavy fraction becomes more and more rapid until the atomic weight of the residue increases to the mean value, and then decreases until the curve finally becomes parallel to the X-axis. *Thus the upper part of the curves for neon, hydrogen chloride, etc., have the form of the curve for lithium.* However, the cut necessary to attain the region where such substances exhibit a curve concave to the X-axis, is so great as to be practically impossible to secure.

78. SYSTEMATIC FRACTIONATION.

The total efficiency of a system of fractional separations of isotopes depends upon: First, the efficiency of the process used, and second, upon the fractionation plan or scheme. An ideal plan of operation is one in which there is no mixing of isotopic materials which have already been separated, but it is easy to see that

FIG. 36.



Increase in the relative density of various isotopic mixtures as the cut increases. The figure covers all of the region accessible to experiment at the present time, but it is of interest that the upper part of all of the curves is similar to that for lithium, which approaches as a limit the line 0.010. The limits approached by the other curves are much higher, but are all lines parallel to the X-axis.

this is never attained. The most nearly ideal *scheme* used thus far is that of Harkins and Madorsky for the separation of mercury as illustrated in Table XLII (Section 73), and that of Mulliken used in connection with his evaporative-diffusion. It will be seen that in one operation, as illustrated in Table XLII, the sample is divided into 8 fractions, three are lighter, and four heavier than ordinary mercury. The apparatus used for this work is such that *any number of fractions may be collected in a single*

operation, so the loss of efficiency by mixing may be made as small as is desired. If the fractions are made too small the number of samples of mercury may, however, become inconveniently large.

The most desirable fractionation scheme is not always the most efficient, since convenience in operation and speed are two very important factors. Thus Harkins and Broeker found it convenient in diffusing hydrogen chloride to make repeated cuts of 20 on the heavy fractions and cuts of 2 on the light fractions. Mulliken, in his application of the method of evaporative-diffusion (Section 75), in which the light fraction diffuses through the wall of a large tube of filter paper, finds that the best plan of operation for this apparatus is to allow 30 per cent. of the vapor passing up into the paper tube to diffuse through its walls. This corresponds to a cut of 1.428, the purpose of the small cut being to give a considerable decrease in the density of the diffusate, which amounts to 26.2 parts per million provided the efficiency of the process is 100 per cent. The corresponding increase in the density of the residue is 11.22 parts. Table XLIV shows the decrease in density of the instantaneous and total diffusates and the increase in density of the residue in operations of this kind. In Mulliken's process the mercury in the distillation flask becomes continuously heavier, and so would decrease in volume and weight. In order to prevent this decrease as much as possible, other heavy fractions are added to the residue. Thus if a specific experiment is begun by the use of ordinary mercury, it will be seen, for example, that when 30 per cent. of the residue has been diffused, the remaining 70 per cent. has a density 11.2 parts per million higher than that of ordinary mercury, so the volume of the mercury in the residue is increased to its initial value at this point by the addition of mercury already prepared of this same density. If the next higher density in stock happens to be 22 parts per million high, then this material is added to the residue in the flask by means of an inlet tube. The operation is stopped only after no outside heavy fractions remain to be added, and the volume of mercury in the flask becomes so low that the apparatus cannot well be operated. It can be seen that this scheme of operation is exactly that used by Harkins and Madorsky, with the exception and added advantage that the volume of the residue can be easily

increased, which is not possible with the large steel apparatus as used at present. However, a tube for the addition of mercury can easily be added to the steel apparatus, so that the general plan of operation of the two forms of apparatus can be made the same.

TABLE XLIV.

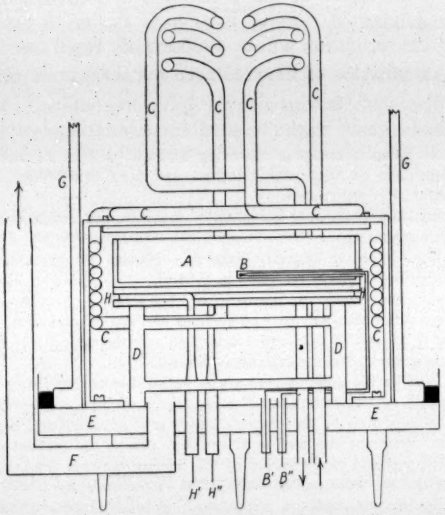
Change of the Density of Mercury in a Diffusion Process of 100 Per Cent. Efficiency (on the Basis of the Value 0.0063 for the Separation Coefficient.)

Fraction in Diffusate.	Cut.	Increase of Density in Parts per Million. Diffusate		
		Residue.	Total.	Instantaneous.
0.00		0.00	−31.4	−31.4
0.02	1.0204	0.64	−31.2	−30.8
0.04	1.0417	1.28	−30.9	−30.1
0.06	1.063	1.95	−30.6	−29.4
0.08	1.087	2.64	−30.3	−28.8
0.10	1.111	3.32	−29.9	−28.1
0.12	1.136	4.02	−29.5	−27.4
0.14	1.163	4.75	−29.2	−26.6
0.16	1.190	5.49	−28.8	−25.9
0.18	1.220	6.25	−28.5	−25.1
0.20	1.250	7.02	−28.1	−24.4
0.22	1.282	7.82	−27.7	−23.6
0.24	1.316	8.65	−27.4	−22.7
0.26	1.351	9.42	−27.0	−22.0
0.28	1.389	10.34	−26.6	−21.1
0.30	1.429	11.22	−26.2	−20.2
0.32	1.471	12.13	−25.8	−19.3
0.34	1.515	13.08	−25.4	−18.3
0.36	1.563	14.03	−25.0	−17.4
0.38	1.612	15.01	−24.5	−16.4
0.40	1.667	16.07	−24.1	−15.3
0.42	1.724	17.13	−23.6	−14.3
0.44	1.786	18.25	−23.2	−13.1
0.46	1.852	19.39	−22.8	−12.0
0.48	1.924	20.60	−22.3	−10.8
0.50	2.00	21.80	−21.80	−9.6
0.75	4.00	43.5		+12.1
0.875	8.0	65.2		33.8
0.9375	16.0	87.2		55.8
	100	145.1		114
	1,000	217.7		187
	10,000	290		259
	100,000	362		331
	1,000,000	435		404

79. SEPARATION OF ZINC AND CADMIUM INTO ISOTOPES.

Work on the separation of zinc into isotopes is now under way in this laboratory, and it is probable that in the preliminary experiments of Harkins and Buckner a separation of 0.04 to 0.05 unit of atomic weight has been attained, when the method of operation and the theory of the process have been taken into account. The conditions necessary for efficient operation have

FIG. 37.



Apparatus for the separation of zinc and cadmium into isotopes. *A*, trough for zinc; *B*, thermoelement; *B'*, *B''*, connections for thermoelement; *CC*, cooling coils; *DD*, glass or porcelain supporting stand; *EE*, steel base; *F*, connection to mercury condensation vacuum pump; *GG*, glass bell jar; *HH*, heating coils; *H'*, *H''*, leads to heating coils.

been so well determined by the study of mercury that the only difficulties in the process are the mechanical ones. The zinc is heated electrically in a moderately good vacuum inside a glass apparatus, and condensed on a chilled surface only about 5 mm. from the surface of the metal when the trough is full of zinc. The capacity of the apparatus (see Fig. 37) is two kilos of zinc (or anything less) for a single run. In a single run with this apparatus an atomic weight difference of 0.067 unit should be

given if on working with one kilo of zinc a 250-gram light and a 62-gram heavy fraction are obtained. Atomic weight determinations will be delayed until it is believed that the separation is 0.3 unit or more of atomic weight.

Similar experiments on the separation of cadmium into isotopes have been begun by Mr. A. A. Sunier and the writer. The isotopic composition of cadmium is unknown, but from the facts that its atomic number is even, and that it lies in the middle of the region of many isotopes, it is extremely probable that the number of isotopes is as high as five or six or more, and that the separation will be a moderately rapid one.

80. CLASSIFICATION OF METHODS USED FOR SEPARATING ISOTOPES.

Mulliken and Harkins give the following outline of the principal methods which might be used for separating isotopes.[110]

I. Methods using phenomena involving thermal motion of molecules and dependent on molecular velocities and their distribution. Separation necessarily incomplete.

1. Equilibrium practically complete[111]—pressure and temperature constant throughout the system—inappreciable separation.[112]

A. Distillation at ordinary pressure, solution or precipitation, liquid diffusion, chemical reactions in general.

2. Equilibrium under a pressure or temperature gradient—degree of separation proportional to logarithm of ratio of pressures or temperatures at ends of gradient, which ratio may theoretically be made indefinitely great, but practically is limited.

A. Equilibrium under a pressure gradient, due to gravity or rapid rotation,[110] or electron impact,[113] etc.—degree of separation proportional to the logarithm of the pressure ratio; or for centrifugal separation, to the square of the peripheral velocity, also to the product of the mol-fractions and to the square of the interval between the atomic weights of the two isotopes, but *independent of the molecular weight.*

B. Equilibrium under a temperature gradient (thermal diffusion[114])—degree of separation approximately proportional to the logarithm of the temperature ratio; also to the product of the mol-fractions, to the square of the difference of the molecular weights of the two isotopes, and *inversely proportional to the molecular weight.*

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[110] Compare Lindemann and Aston, *Phil. Mag.*, [6] **37**, 523 (1919), who discuss in particular, methods I, 1; I, 2, A; and II, 1.

[111] Compare Lindemann and Aston, Ref. 27; Lindemann, *Phil. Mag.*, [6] **38**, 173 (1919); Soddy, Ref. 21.

[112] A photochemical method of separation has been tried by Merton and Hartley [*Nature*, **105**, 104 (1920)] but was unsuccessful.

[113] Skaupy: *Z. Physik*, **2**, 213 (1920).

[114] Chapman: *Phil. Mag.*, [6] **38**, 182 (1919).

3. Non-equilibrium processes. Flow under a gradient of partial pressure or concentration. The maximum efficiency of separation in A, B, and C, is given for zero partial pressure at the lower end of the gradient. The degree of separation in A, B, and C, is definite and limited for the light fraction, but proportional to the logarithm of the cut for the heavy fraction; while for both fractions it is proportional to the product of the mol fractions (as in thermal diffusion).

A. Molecular effusion and non-equilibrium evaporation.[115]

B. Molecular diffusion.

C. Interdiffusion of gases.

D. Initial effects in evaporation, diffusion, etc.

II. Methods using phenomena in which molecules act as independent masses—separation almost complete.

1. Positive ray methods[116]—yields very small, though products are, theoretically, almost pure.

2. Possibly, electrolysis of ionized liquid or gas (separation probably difficult or impossible, because mobility of isotopic ions is probably practically equal; slight differences of mobility will be masked by diffusion and convection).[116]

81. THE TRACKS OF ALPHA PARTICLES IN GASES.

The photographs of the tracks of alpha particles secured by C. T. R. Wilson [117] by the use of his cloud track apparatus are of considerable interest in connection with the study of the structure of the atom. Some of the tracks indicate that an alpha particle is occasionally turned very sharply from its initial path, presumably by approaching very closely to the nucleus of an atom, as is evidenced by the sharp spurs which result. Shimizu [118] has devised a modification of this apparatus which gives two expansions per second of the chamber which contains the water vapor. Thus two complete sets of alpha ray tracks can be observed visually, or photographed, every second, so that 7200 photographs can be secured in a single hour of operation.

[115] The method of irreversible condensation of a vapor or gas in a special case of the method of molecular effusion, and is thus somewhat similar to irreversible evaporation. J. J. Thomson's suggestion [*Proc. Roy. Soc.*, **99A**, 87 (1921)] that the isotopes of chlorine might be separated by fractional absorption of hydrogen chloride in an alkaline solution would make use of this method. This would hardly be practical, however, due to the rapidity of the absorption and the consequent impossibility of good mixing. If air were admixed with the hydrogen chloride, there might be some degree of separation as a result of gaseous diffusion.

[116] See also Lindemann, *Proc. Roy. Soc.*, **99A**, 87 (1921).

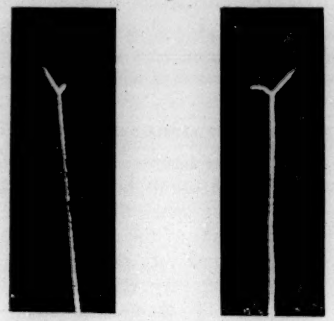
[117] C. T. R. Wilson: *Proc. Roy. Soc.*, **A87**, 1277–92 (1922).

[118] Shimizu: *Ibid.*, **99**, 425–35 (1921).

With this apparatus Shimizu made the interesting observation that about one in three hundred of the alpha ray tracks is *branched* at the end, as in Fig. 38.

Mr. R. W. Ryan and the writer have constructed two models of the Shimizu apparatus, one with an expansion chamber 8 cm. in diameter, and a much larger apparatus in which the diameter is 13.3 cm. The smaller apparatus is shown in Fig. 39. With this many branched tracks have been found, but their relative number does not seem to be so great as that found by Shimizu. Fig. 40*a* shows 9 or 10 quite straight tracks from a single source,

FIG. 38.



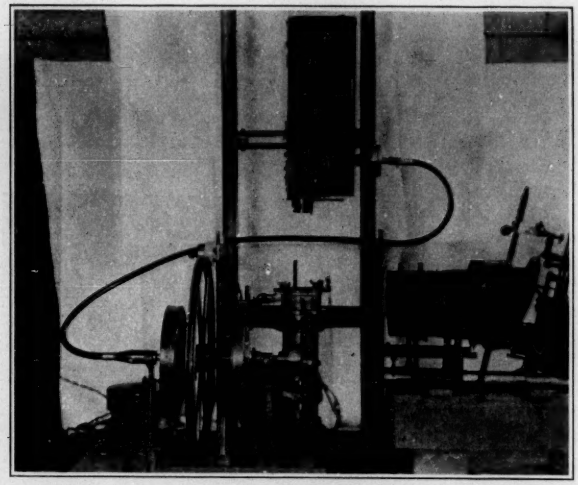
Photograph of a branched α-ray track viewed from two positions at right angles to each other as taken by Shimizu. Actual magnification 5.5.

with one track at right angles that represents an alpha particle which was later in crossing the field of view than two of the other alpha particles. It will be seen that when this occurs the tracks of the particles which shoot through earliest reduce the supersaturation of the water vapor to such an extent that the particles which pass later leave no visible tracks in their immediate vicinity.

Fig. 40*b* represents one alpha particle which was turned through a sharp angle very close to the source, and another which gives a branched track at the end, though the branching may not show clearly in the reproduction. Fig. 39*c* is of considerable interest since it gives a branched track, one of the branches of which is about 2 centimetres long. Unfortunately this photograph was taken in only one plane, so it is impossible to determine the length of the other branch. That some alpha particles are turned

through as much as a right angle may be seen in Fig. 40*d*, while 40*e* shows a branching which occurs near the source of the particle. Figs. 40*f* to 40*i* are typical sets of tracks taken from the series of several thousand photographs thus far secured. A number of lenses have been tried, and the best results secured by

FIG. 39.



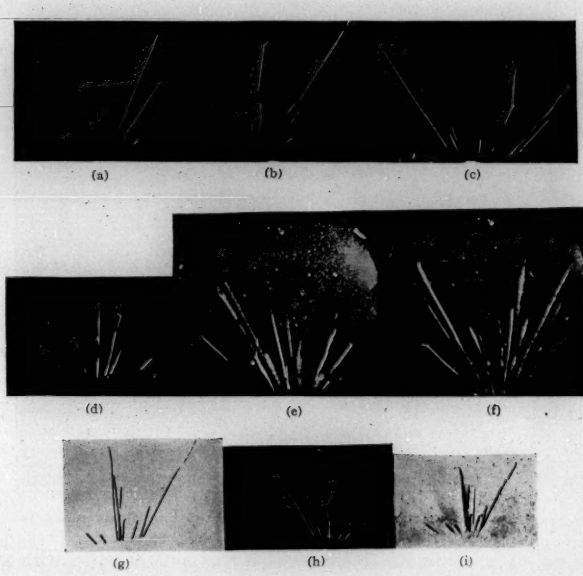
Apparatus for photographing the tracks of alpha particles. (Shimizu-Wilson apparatus as modified by Ryan.)

the use of a Cooke F2 cinematograph lens in connection with a Universal Moving Picture Camera.

The interest in the branched tracks lies in the idea that while one branch may be due to the alpha particle projected by the radioactive source (polonium in these specific experiments, though radium-C will be used later), the other branch is probably due either to the atom nucleus which is hit, or to an alpha particle which is disrupted from the nucleus. It is hardly probable that it can be due to a disrupted H-particle (proton) since the path of such a light particle should be much longer. If it can be proved that an alpha particle is disrupted from the nucleus in any of these

branchings of the path, the result would be of extreme importance since thus far there is not the slightest evidence that anything other than hydrogen has been produced in the *artificial* disruption of atoms, though it is well known that helium is produced in the *natural* disintegration of the radioactive elements. Both Shimizu

FIG. 40.



Alpha ray tracks in air. The actual full length tracks are about six cm. long, so the reproductions are from one-third to one-half natural size. These photographs have not been retouched.

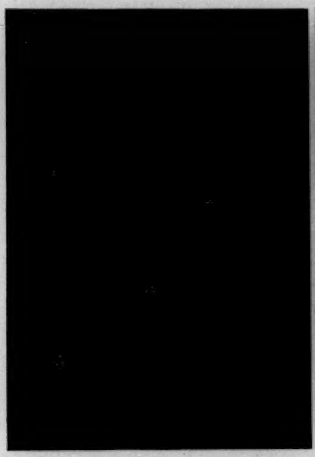
and Rutherford have in mind the idea that these branched tracks may be an indication that the nucleus of the atom is disrupted.[119]

A single run of 4000 photographs, as made in this laboratory, gave about 25 tracks which spread into two branches at the end. In one of these a remarkable branching occurred (Fig. 41), since

[119] The work of Mr. Ryan and the writer has been greatly delayed by the lack of a good lens for this work, but the lens now in use is well adapted for this purpose.

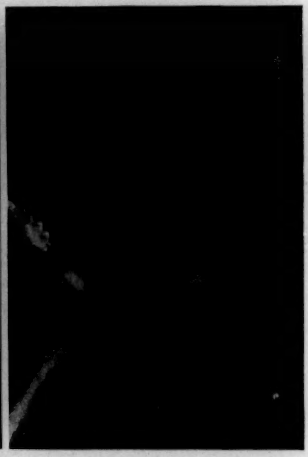
one of the tracks is shot almost directly backward (actually turned through an angle of 130° instead of 180°) while the other is at an angle of about 20°. In the projection on the photograph the angle of incidence and of reflection are almost equal. Such tracks are of great importance in the study of the problem, but a large number of them must be secured before definite conclusions as to their meaning are warranted. It seems probable,

FIG. 41.



Alpha ray track with forward and backward branches (Ryan and Harkins).

FIG. 42.



Alpha ray track with right angle turn.

however, that the forward track is due to an oxygen or nitrogen nucleus and the backward track to the deflected alpha particle. The kinetic energy of the alpha particles given off by some of the radioactive substances is so extremely great that it seems difficult to conceive that even nuclei built of alpha particles alone will resist disruption in all cases. However, the number of disruptions may possibly be so small that no statistical evidence of their occurrence can be obtained by the use of the present form of apparatus, which, while it possesses the great advantage that it makes almost the whole of the track of the alpha particle visible,

has also the great disadvantage in comparison with Rutherford's scintillation method, that the cloud track method cannot be used when the number of alpha particles is large. In the scintillation method, on the other hand, millions of alpha particles per second may be used, since the screen used is placed beyond the range of all of the alpha particles used as projectiles.

Mr. Ryan and the writer have observed a number of longer range tracks which occur when the alpha particles pass through paraffin. These seem to have a different appearance from the ordinary alpha ray tracks. On account of the lack of a sufficiently powerful radioactive source, it has been impossible to determine whether these are caused by H-particles or not. If they should prove to be such particles it would be possible to demonstrate photographically the disintegration of elements of the type of aluminium and nitrogen. The H-particles produce a smaller ionization than alpha particles.

Interesting experiments by Kenoshita, Ikeuti, and Akiyama,[120] made with the original Wilson apparatus, give photographs in which two alpha ray tracks originate at a common point in the gas of the apparatus. Each point represents the position of an atom of actinium emanation which at the moment disintegrates into AcA, and 0.002 second later into AcB.

82. THE BUILDING AND EVOLUTION OF ATOMS.

Early in 1915 Harkins and Wilson published the first definite theory that the nuclei of light atoms are built up from alpha particles and hydrogen nuclei (positive electrons). The present paper reviews their theory and presents the experimental evidence collected by the writer in its favor. This evidence is so comprehensive that it cannot well be summarized in this section, but it may be noted that the figures and tables of the present paper [121] give the most conclusive evidence, presented *prior* to the disintegration of certain light elements into hydrogen, that the principal group involved in the building of the light atoms is the alpha particle. It is the opinion of the writer that not only is this true, but that at the present time *the experimental chemical data*

[120] Tracks of α-particles emitted by actinium emanation and actinium A. S. Kenoshita, H. Ikeuti and M. Akiyama, *Proc. Phys. Math. Soc. Japan*, **3**, 121–33 (1921) *Sci. Abs.*, **25A**, 52, (1922).

[121] Particularly in Figs. 12, 13, 14, 19 and 21, and in Tables XXVI, XXVII, III, IV, XII, XXII, XXIII, and XXIV.

summarized here give much more conclusive evidence for the building of the light atoms from alpha particles than the disintegration experiments themselves. That this is the case will be realized by anyone who makes the considerable effort necessary to thoroughly digest the great mass of evidence presented. The fact that the light elements give exactly the same form of "map" (Fig. 19) as the radioactive elements; the fact that Fig. 12 exhibits periodicities of 2 and of 4 in both directions, these being the value of the charge and mass of the alpha particle; and the importance of the numbers 2 and 4 in the abundance relations of the elements and atomic species, give the strongest, though possibly not the most simple, evidence for this point of view.

The theory is essentially one of the building and evolution of the atomic species.[122] It differs from the theory of Nicholson which preceded it in that it can find no place thus far for the hypothetical elements coronium, nebulium, protofluorine, etc., but makes use of a known element, hydrogen, as its fundamental building stone, and of a second known element, helium, as the

[122] Aston (page 116, "Isotopes") classifies the writer's theory as a "disintegration" as opposed to the more "attractive (evolution) theory," thus showing that he has not read even the titles of the first papers of the series. Thus he has missed the statement in the second paper (1915) "the evidence presented in these papers, which seems to show that the elements are atomic compounds of hydrogen and helium, appears to give some support to the theory of the evolution of the heavier atoms from those which are lighter." The third paper of the series (published in 1916 and again in 1917) is entitled "The Evolution of the Elements and the Stability of Complex Atoms," and another paper published at the same time was entitled "The Building of Atoms." It is my own opinion that Aston underestimates the effects of the atomic disintegrations, but his classification of the writer's viewpoint as a disintegration, as opposed an evolutionary theory, is altogether incorrect as the above titles show. His statements as to the success of predictions of the existence of isotopes, as given on page 117, are equally incorrect and misleading. It is unfortunate that Aston believes that the ideas of evolution and of disintegration are altogether opposed and exclusive of each other, since the more rational viewpoint is that both are of prime importance. The writer has felt that the nuclei of light atoms have been mostly built up from alpha particles and hydrogen nuclei, but it is not a necessary conclusion that all light atoms are permanently stable just because they are built from a relatively small number of particles. In fact, Fig. 21 and other similar figures of the present paper indicate that the stability of the light atoms decreases very much more rapidly than that of the heavy atoms when they depart from the region of stability by a certain number of neutrons (*pe*).

most important secondary unit. It agrees in general with the astronomical theory of the evolution of the elements from lighter to heavier, in the stars, though it is much more specific and is based upon much more extensive evidence than the astronomical theory. The bearing of the astronomical evidence is much more in doubt, since the changes in the spectra of the nebulæ and the stars, in which hydrogen and helium are supposed to appear first, and then to change gradually into calcium, magnesium, oxygen, iron, etc., might possibly be due to the conditions of excitation of the spectra and the segregation of the elements in these bodies. Also the evolution of the stars may not be in the supposed order. The writer is not opposed to, but rather is in favor of, the astronomical theory of evolution, but it is nevertheless of importance to point out that the evidence which it presents in this connection is as yet faulty.

The importance of the writer's whole number rule for the atomic weights of the elements other than hydrogen is now well recognized. When taken in connection with the theory of relativity it indicates, as was first pointed out in 1915 by Harkins and Wilson, that the *only* source of enormous amounts of heat (other than that of radioactive changes) such as would account for the excessive amount of heat given off by the sun and by the giant stars, is to be found in the union of hydrogen to form helium, which, for one pound of hydrogen, gives an amount of energy corresponding to that liberated in the combustion of 10,000 tons of coal.[123]

Department Store Laboratory.—E. B. MILLARD (*Jour. Ind. Eng. Chem.*, 1922, xiv, 785–786) gives a resumé of the work done in the chemical laboratory of a department store. The routine work consists chiefly of determinations of the wool or silk in materials, and especially the detection of artificial silks, also tests of the fastness of dyed fabrics to perspiration, sunlight, washing, or water spots. The coal used in the power plant, and the milk used in the restaurant are analyzed at frequent intervals. The laboratory also makes examinations in connection with the adjustment of claims of unsatisfactory materials. New materials are analyzed as they appear on the market. The information obtained is placed at the disposal of both the purchase and the sales divisions of the organization. J. S. H.

[123] For the calculation of the amount of energy liberated see section 22 of the present paper.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THEORY, CONSTRUCTION, AND USE OF THE PHOTOMETRIC INTEGRATING SPHERE.[1]

By E. B. Rosa and A. H. Taylor.

[ABSTRACT.]

DURING the last fifteen years great progress has been made in the production and utilization of light. With this progress has come the necessity for greater precision in the measurement of light output, and the Ulbricht photometric integrating sphere has been extensively utilized for this purpose. It is the only available instrument by which the total light output of sources can be determined in one measurement. There is no complete treatment of the theory, construction, and use of the sphere available in English. This paper has been written to meet that need, and should be of interest to all who are concerned with photometry.

The majority of the spheres in use to-day are built of shaped sheet metal segments fastened to structural steel. Such spheres can be made of fairly light but substantial construction, but they are expensive to build. In the smaller sizes a cheaper construction may be realized by the use of papier-maché globes such as are used in schools.

In 1915 the authors designed and constructed an 88-inch reinforced concrete sphere at the Bureau of Standards. Steel T-rails were shaped into circular arcs and fastened to metal rings at each end, thus forming ribs of a spherical framework. These ribs were fastened together with metal bars and expanded metal lath, and the whole was plastered with concrete in the proportion of one part Portland cement to two and one-half parts sand. The interior was swept out to a true spherical shape by means of a special sweep hinged at the centre of a pipe placed on the vertical diameter of the sphere. Later both interior and exterior surfaces were finished with white cement, giving a wall about one to one and one-half inches thick. A concrete sphere such as this, especially in the larger sizes, can probably be constructed more economically than a metal sphere of the same size.

* Communicated by the Director.

[1] *Scientific Papers*, No. 447.

This sphere has been thoroughly tested and found to give accurate results for many types of light sources. The sources tested included vacuum lamps both bare and with several types of glass reflectors and globes and a metal reflector. In all cases the agreement of the results with those obtained by point-by-point integration was practically within the range of ordinary errors of photometric measurements. Considerable care is necessary in the use of the sphere for measuring light sources which differ appreciably in their absorption of light, and in order to obtain reliable results on such sources proper corrections must be determined and applied.

The requirements for a satisfactory paint for photometric spheres are rather severe, and since no commercial paints fulfilling these requirements could be found, it was necessary to develop one. A good paint for this purpose is composed of alcohol, camphor, celluloid, and zinc oxide. It has a very high reflection factor, and does not discolor with age. The photometric equipment consists of a bar photometer, Lummer-Brodhun contrast photometer head, sectored disks, recording drum, and magnet, etc. The " substitution " method of photometry is used.

The theory of the sphere has been investigated, and tests have been made to verify certain phases of it, with satisfactory results. The best size and position of the opaque screen have been theoretically determined. It is found that as the lamp approaches the sphere wall at a point screen from the observation window, the brightness of the latter is reduced. This is due to the fact that as the lamp approaches the wall more of the direct light flux falls on the zone screened from the observation window, and hence it must be reflected from the sphere wall at least twice before it can reach the window.

One source of error in the use of such spheres is often overlooked. If the lamp being tested is somewhat blackened, or has parts which absorbed a considerable portion of light, the amount of light which it absorbs in the sphere will increase as it approaches the sphere wall. The amount of light absorbed by the lamp is also greater when the reflection factor of the sphere walls is high. These facts are of great importance if life-test lamps, appreciably blackened, are being photometered. It can be shown theoretically that a sphere to be used for life-test measurements of incandescent lamps should be painted with a paint having a reflection factor

of about 80 to 85 per cent. in order to minimize the errors of measurement.

The theory of the sphere assumes that its surface is a perfect diffuser, that is, that the specific brightness of any area is independent of the angle of view. Measurements of the diffusion characteristics of the sphere paint and the milk-glass observation window have been made. These show that the error arising from the measurement of a narrow beam of light in terms of a perfectly diffused light, or of light uniformly distributed in the sphere, is practically zero when the beam is directed at the sphere wall at a point about 80° on the circumference from the window.

The original paper also contains a bibliography of the subject.

PROPERTIES OF ELECTRICAL INSULATING MATERIALS OF THE LAMINATED, PHENOL-METHYLENE TYPE.[1]

By J. H. Dellinger and J. L. Preston.

[ABSTRACT.]

THE manufacture of phenolic synthetic resins as applied to the fabrication of electrical insulating material has only become commercially important within the last twenty years. Three men might be mentioned who have been instrumental in the development of these resins and the resulting insulating material in this country, namely, Messrs. Jonas W. Aylesworth, Leo H. Baekeland, and L. V. Redman.

This type of insulating material was developed to meet a real commercial need. Experience had shown that insulating materials using shellac, bituminous and similar materials as a binder, and hard rubber, hard fibre, glass, porcelain, amber, celluloid, and other materials had certain mechanical or electrical defects. The phenolic insulating materials were developed to correct some of the major weaknesses inherent in the other types, but to the conservative investigator the phenolic materials are not believed to be a panacea for all insulation troubles. These phenolic materials, as an example, are not substitutes for hard rubber though they are advantageously used to replace hard rubber in many places. Hard rubber softens, warps, and discolors when left in the sunlight or exposed to moderate heat. The phenolic materials apparently do not. The price of the better grades of hard rubber is already quite high and is increasing, while the price of phenolic insulating

[1] *Technologic Papers*, No. 216.

materials should decrease as the knowledge of the art increases. Properly made and properly protected hard rubber is superior electrically to the phenolic materials. The average value of phase difference, that is, the dielectric power loss, for the phenolic insulating materials, is four to eight times that for hard rubber. The phenolic synthetic resins have a wide variety of uses in many fields, including the manufacture of decorative beads, cigarette holders, noiseless gears, sword scabbards, and conductor tubes in vinegar factories. It is, however, in the manufacture of electrical insulating materials that they find one of their most important applications.

The materials manufactured using the phenolic synthetic resins may be broadly classified as laminated materials, or moulded materials. As indicated by the title, this paper is concerned exclusively with materials of the laminated type. Unlike the laminated materials, the moulded materials can be formed into intricate shapes without machining. They therefore have a wide variety of applications. It is expected that a publication supplementing this paper will be published later, giving some data on moulded materials.

The materials referred to in this paper as of the laminated, phenol-methylene type are those made by building up sheets of paper, fibre, or fabric, which had been previously impregnated or coated with phenolic (synthetic) varnish to some desired thickness and then subjecting the stack to comparatively great pressure in a heated hydraulic press. The varnishes used in the manufacture of these materials were Bakelite, Condensite, and Redmanol, manufactured respectively by the General Bakelite Company, Condensite Company of America, and The Redmanol Chemical Products Company. These varnishes are all somewhat similar in that they depend on chemical reaction and are all synthetic. The chemical reaction of the varnish is retarded so that it can be shipped to the consumer or stored for some time (the length of time depending on the type of varnish). When the varnish is subjected to heat, the reaction is again started and tends toward completion at a rate depending on the temperature. This heating is done after the filler (paper, etc.) has been impregnated or coated with the varnish and the stack placed in the press. The pressure (with heat) has a tendency to produce from the separate sheets, a dense homogeneous sheet of insulating material.

This paper is meant to serve as a compilation in a form convenient for reference on the electrical, mechanical, chemical and thermal properties of the laminated sheet insulating material of the phenol-methylene type manufactured in the United States; on the methods of testing the electrical, mechanical, chemical and thermal properties; and on books, periodicals, and patents dealing with tests on or properties of insulating material.

Radio-frequency phase difference or power loss, dielectric constant, and flashover voltage, direct current surface resistivity and volume resistivity, tensile strength, modulus of elasticity (tensile), proportional limit, modulus of rupture, modulus of elasticity (transverse), Brinell hardness, scleroscope hardness, impact strength, permanent distortion, density, moisture absorption, machining qualities, thermal expansivity, and the effects of heat, acid, and alkali have been considered in this paper, and data or statements are given relative to these properties. Other data are also given which have not been determined at this Bureau. These data include values on dielectric strength or puncture voltage, crushing strength parallel with and perpendicular to the laminations as well as moisture and oil absorption when the time of immersion was longer than in the Bureau of Standards tests.

Much space in this paper is devoted to the description of the methods of testing. This seems quite necessary because some of the numerical data are in part a function of time, voltage, pressure, etc., as well as of the mechanical arrangement of the testing apparatus. Such a description of testing methods serves other purposes. Many of the methods were developed at the Bureau of Standards after much experimental work. The methods are described in detail so that they may be available to others who wish to do such testing, and with the hope that constructive criticism may be stimulated which will result in improved methods.

A part or all of the above-named tests have been made on fifteen grades of laminated, phenolic insulating material as manufactured by the four manufacturers in the United States. The manufacturers of the several grades are given in the following alphabetical order:

Diamond State Fibre Company.—Condensite Celoron: grade 10, fibre base; grade 15, fibre base; grade 20, fabric base.

The Continental Fibre Company.—Bakelite-Dilecto: grade XX, paper base; grade X, paper base; grade C.B., fabric base.

The Formica Insulation Company.—Formica: grade M, paper base; grade M-2, paper base; grade P, paper base; grade R, fabric base.

Westinghouse Electric and Manufacturing Company.—Bakelite Micarta: grade 32-X, paper base; grade 21-X, paper base; grade 323, paper base; grade 213, paper base; grade 21-D, fabric base.

These grades cover all that were in general use at the time this research was started. Other grades have appeared since, but as a rule they are not fundamentally different from some one of the grades reported in this paper.

The data are arranged in such a manner that it will be directly usable by persons having different problems involving this type of insulating material.

First, there is a detailed record of data for all thicknesses of all makes and grades of material considered in this paper. This should assist the engineer in determining the effects of various electrical or mechanical stresses applied to the material or the effects of changes in the material on the electrical or mechanical properties. As an example this paper should assist him in determining the probable effect on phase difference or power loss of the season of the year, baking or drying, frequency variation, thickness, color or dye, and surface finish. He could also get an idea of the effect of the grain of the insulating material on tensile and transverse strength properties. Many other examples might be given of the use of the detailed data.

Second, the data have been summarized. In this summary the data on the various materials, grades, and thicknesses have been kept separate. It is somewhat similar to the detailed record except that the results of many measurements on any one sample have been averaged and recorded.

Third, here the detailed data have been averaged and recorded regardless of thickness. This gives the engineer a general idea of the individual characteristics of the various makes and grades. It is a very condensed summary.

Fourth, a summary-comparison table has been prepared and included in this paper. Average values for the various properties of laminated phenolic insulating materials are given regardless of make, grade, or thickness. In this same table the properties of hard rubber, hard fibre, laminated phenolic, and moulded phe-

nolic materials have been recorded in a manner to show how they compare. For one desiring only very general information, this table should be quite useful.

RESULTS OF SOME COMPRESSION TESTS OF STRUCTURAL STEEL ANGLES.[1]

By A. H. Stang and L. H. Strickenberg.

[ABSTRACT.]

THIS article presents the results of compression tests of 170 structural angles, made at the Pittsburgh branch, Bureau of Standards. The object of the tests was to determine the ultimate compressive strength of angles fastened at the ends in such ways as would closely correspond to their connections in the construction of transmission towers. There was also tested a series of angles with square ends. An end fixation factor was found to represent satisfactorily the effect of different types of end connections.

The values of the maximum unit load in these tests vary over a considerable range for any given slenderness ratio and manner of fastening the angles in the testing machine.

In most cases the specimen which sustained the greatest unit load for a given slenderness ratio and method of fastening suffered the least lateral deflection and the angle which bent most sustained the lowest unit load at failure, the deflection being measured at 4/9 of the theoretical maximum load.

For large slenderness ratios the average values are well represented by Euler's formula for long columns, calculated for different values of the end fixation factor.

The Kármán curves, recalculated for a yield point of 37,000 lbs./in.^{2} and modulus of elasticity of 30,000,000 lbs./in.^{2} represent the average results for small slenderness ratios for several methods of end fixation, except in the neighborhood of $l/r = 80$ to 85, where the effect of eccentricity was greatest. The values of the end fixation factor are given.

For angles with ends folded the column formulas considered do not represent the results found in this series of tests.

It is believed that the values of end fixation factor are of importance in the design of structures where the end conditions

[1] *Technologic Papers*, No. 218.

approximate those used in these tests, no matter what formula the designer prefers to use.

Eccentricity of loading produces a diminution of column strength. In these tests the greatest effect of eccentricity was observed in the neighborhood of a "free length" corresponding to $l/r = 85$, which agrees with the results of Kármán's investigations.

TEST OF A HOLLOW TILE AND CONCRETE FLOOR SLAB REINFORCED IN TWO DIRECTIONS.[1]

By W. A. Slater, Arthur Hagener, and G. P. Anthes.

[ABSTRACT.]

A LARGE slab, 48 by 115.5 ft. centre to centre of outer supporting girders, was loaded. In the 48-ft. dimension the slab was divided into three spans of 16 ft. each. In the 115.5-ft. dimension it was divided into six spans, two end spans were 16 ft. each, the two middle spans 19.25 ft. each, and the two spans at the other end were 22.5 ft. each. The slab was therefore divided into 18 panels, of which six panels were 16 ft. square, six panels were 16 by 19.25 ft., and six panels were 16 by 22.5 ft. Girders extended along all panel edges, and columns stood at all intersections of girders. The slab was 6 in. thick over all and was made up of 6 by 12 by 12 in. clay tiles laid in rows parallel to the panel edges with ribs of concrete 4 in. wide and 6 in. deep between rows of tiles in both directions. Each concrete rib was reinforced with one ½-in. round bar in the top for negative moment and with the same in the bottom for positive moment. The bars for negative moment extended out into the panel one-fourth of the span length in the direction of the bar and were there hooked for anchorage.

The slab reinforcement had a yield point of about 54,000 and the girder reinforcement of about 46,000 lb. per sq. in.

According to current methods of design the working loads (sum of live and dead loads) for the three sizes of panel would be 83, 67 and 48 lb. per sq. ft. for the square, intermediate-size, and long interior panels, respectively. The weight of the slab was approximately 50 lb. per sq. ft.

For about two months the square panels stood under a uni-

[1] *Technologic Papers*, No. 220.

form load (sum of live and dead loads) of about 450 lb. per sq. ft., the intermediate-size panels under 330 lb. per sq. ft., and the long panels under 280 lb. per sq. ft. The load was then shifted and (with smaller loads on adjoining panels) the loads for the succeeding six months on certain panels were: square panels, 780; intermediate-size panels, 655, and long panels, 555 lb. per sq. ft. Finally the load was concentrated still more and for about eleven months the loads on single panels of each size have been: square panels, 1463; intermediate-size panels, 1234, and long panels, 970 lb. per sq. ft.

During the loading strain gage readings of elongation and shortening were taken at about 1600 critical places in the concrete and in the reinforcement. The negative moments for the 16-ft. spans of the interior panels based upon these stresses (observed after maximum uniform loads of 450,330, and 280 lb. per sq. ft. had been in place about two months) with an allowance for dead load stresses, were 0.0186 *Wl* for the square panels, 0.0277 *Wl* for the intermediate-size panels, and 0.0398 *wl* for the long panels. The negative moment in the direction of the long span was 0.0213 *Wl* for the intermediate-size panels and 0.0179 *Wl* for the long panels, where *l* is the short span.

The coefficients for the exterior panels averaged about 20 per cent. greater than the coefficients for the interior panels.

Both the deformations and the deflections increased when the load remained constant over a considerable time, but the fact that so great a load has been carried for so long a time without excessive deflection removes any misgiving as to the adequacy of the form of construction used.

The deflections at the centres of the interior panels observed after the maximum uniform load had been in place about two months averaged 1/273, 1/563, and 1/1800 of the clear short span for the squares, intermediate, and long panels respectively. Upon removal of 80 per cent. of the load the recovery was 50 per cent. of the original deflection or more.

At this stage of the test the largest crack was less than 0.01 in. wide. The largest crack in the under side of the slab under a load of about ten times the design loads stated in a previous paragraph was about 1/40 in. wide.

The points of zero stress in the negative reinforcement occurred at about one-fifth points of the spans.

Under the greatest loads applied the shearing stresses in the ribs of the slab were 405 lb. per sq. in. or more assuming the tile walls to have been effective in resisting shear. If the resistance of the tile walls is neglected the shearing stress must have been 500 lb. per sq. in. or more.

The estimated shearing stress in one of the girders is 440 lb. per sq. in. The loads on which these shearing stresses are based had been on the slab for nearly a year.

THE MAGNETIC SUSCEPTIBILITY AND IRON CONTENT OF CAST RED BRASS.[1]

By L. H. Marshall and R. L. Sanford.

[ABSTRACT.]

THE presence of iron in commercial brass is often objectionable, particularly if it occurs as discrete, poorly alloyed particles. In order to obviate any such harmful effects, a very low ferrous content is frequently specified. Therefore, a rapid, non-destructive method for quantitatively determining its presence would be of great value in practice. A magnetic method of inspection would fulfill the requirements of such a test if a definite relationship exists between some magnetic property and the iron content of the metal. From the meagre information available in the literature it was evident that this matter had received little attention.

With these facts in mind a study was made of the magnetic properties of cast tin red brass contaminated with iron. A series of seven samples of an alloy of the type 82 copper, 15 zinc, 3 tin was prepared containing various small proportions of iron up to 0.75 per cent. These specimens were magnetized in a suitable solenoid. A test coil of 1200 turns extended over two-thirds of the specimen and readings of the magnetic induction were taken by means of a ballistic galvanometer. Greater precision was secured by balancing out the magnetizing force by means of a variable mutual inductance, so that the galvanometer deflection, in each case, was a measure of the increase in flux density due to the specimen (metallic induction).

Magnetic properties were determined in the cast condition and after annealing 15 minutes at 625° C., 8 hours at 800° C.,

[1] *Technologic Papers*, No. 221.

and 16 hours at 800° C. for different values of magnetizing force up to 500 gilberts per cm. The microstructure of the metal was determined before and after these various heat treatments. The cored structure of the cast material largely disappeared after the first eight-hour anneal. The eutectoid present in the cast samples was likewise absorbed at this time. The second eight-hour anneal caused no further change in structure. Oxide inclusions were present in all of the samples. Up to 0.14 per cent. the iron went into solid solution in the matrix of the alloy, but larger amounts than this caused the appearance of pale, rounded areas of an iron rich constituent. A rough estimate of the iron content could be made from the number and size of these areas. The percentage of iron present had no noticeable effect on the grain size of the metal, nor did the grain size have any definite influence on the magnetic properties of the specimens.

The data obtained revealed several interesting points. For instance, the magnetic properties are not a precise index of the iron content of the cast metal. Then the magnetic susceptibility is markedly affected by changes in physical condition produced by heat treatment. Even after the material has been thoroughly annealed, there is still no simple relationship between the magnetic susceptibility and the iron content. The seeming irregularities in the magnetic behavior of these brass samples were probably due, in the case of the cast specimens, to the unhomogeneous structure of the metal; while those of the annealed bars were caused by the presence of the iron as two modifications, the dissolved and the segregated. The iron content was the source of the magnetic effects observed.

RELATIVE USEFULNESS OF GASES OF DIFFERENT HEATING VALUE AND ADJUSTMENTS OF BURNERS FOR CHANGES IN HEATING VALUE AND SPECIFIC GRAVITY.[6]

By W. M. Berry, I. V. Brumbaugh, J. H. Eiseman, G. F. Moulton, and G. B. Shawn.

[ABSTRACT.]

In connection with an investigation conducted by the Public Service Commission of Maryland to determine the most economic heating value standard for manufactured gas in the city of Balti-

[6] *Technologic Papers*, No. 222.

more, the Bureau of Standards conducted an extensive series of laboratory tests to determine primarily: (1) The relative utilization efficiency of gases of different heating value; (2) the extent to which present appliances can be adapted to give good and efficient service with gases of different heating value and composition; and (3) what adjustment in appliances is necessary to give the consumers good and efficient service when different kinds of gases are mixed and there is a variation in the composition, heating value, and the specific gravity of the gas.

After giving due consideration to a number of factors that have an influence on efficiency, it can be stated that the results of the laboratory tests of gases varying in heating value from 300 to 600 Btu per cubic foot indicated that the usefulness for top burner cooking is dependent almost entirely upon the total heating value per cubic foot. Thus, to heat a given quantity of water to the same temperature in the same time required two cubic feet of 300 Btu gas to one cubic foot of 600 Btu gas. In other words, the quantity of gas required varied inversely with the heating value of the gas.

Over the range of usual operating conditions the efficiency of heat absorption varies only slightly with a change in the rate of heat supply. With the star type of burner and an average size vessel, the efficiency varied from about 36 per cent. at 7000 Btu per hour to 37.7 per cent. at 11,000 Btu per hour.

Burners can be operated over a somewhat greater range of adjustment with coal gas than with water gas. The tests show that with coal gas the yellow flame occurs at a higher Btu per cubic foot of mixture (lower air-gas ratio). On the other hand, with coal gas it is practicable to operate burners with a lower Btu per cubic foot of mixture (higher air-gas ratio) without having the burners flash back.

The results on the whole show that present domestic range burners can be adjusted to give satisfactory service over a wide range in heating value, the slight differences in behavior of the different gases not being of sufficient importance to have much weight in any consideration of their relative merits for use in domestic appliances. Some change in size of orifice and air shutter adjustment of burners is necessary to secure the best service when a material change is made in heating value, but

most existing burners can be readily adjusted to give good service with heating values as low as 450 Btu without alterations of the burners.

The practice of mixing different gases has become quite common as a result of the development in coke-oven processes with the production of by-product gas, the building of combination coal and water gas plants, and the necessity of supplementing natural gas with different kinds of manufactured gas. Uniformity in heating value, specific gravity and pressure are essential for the very best service, yet it is practicable to adjust burners to give satisfactory service in cities where different gases are mixed and there is considerable variation in the heating value or specific gravity.

Investigations of Crystalline Structure by Means of X-rays. F. Kirchner. (*Ann. d. Physik*, No. 17, 1922.)—When a substance is obtainable in large, perfectly formed crystals it is possible from the application of X-rays to determine with great exactitude the dimensions of the crystal structure. When, on the other hand, the substance is not so existent the Debye-Scherrer method for powdered crystals may be applied but the accuracy of the results is much less. There is another method, that of Seeman and Bohlin, in which the rays are brought to a focus after reflection from the metal under investigation. Kirchner shows how to improve the technic of this method and how to derive more accurate dimensions by its use. He succeeded in getting data on the structure of copper from .002 milligram of the metal deposited on a sheet of aluminium.

An alloy of iron and nickel containing 25 per cent. of the latter was long ago shown by Hopkinson to possess remarkable magnetic properties. It can be magnetized provided it has been strongly cooled, its permeability then being roughly equal to that of hard nickel. If the alloy be heated to 580° it ceases to be magnetic and remains in this state when it cools down to room temperature. Its permeability is now not much above that of air. The physical properties of the alloy differ in the two states. In the magnetic state its specific electrical resistance is 0.00052, while in the non-magnetic state it is .00072. Similar data for specific gravity are 7.98 and 8.15, and for tensile strength 135 and 80 kg. per sq. mm.

Photographs of the lines formed by the rays after reflection from the alloy are not alike, the number of lines being greater for the magnetic state. All of the lines for the non-magnetic state appear also for the magnetic state. The author interprets this to mean that upon the transition from the non-magnetic to the magnetic state there is a large increase in the number of atomic configurations of a certain kind which were present to only a small extent in the former condition.

G. F. S.

An Analogy between Electrical Waves and X-rays. N. KAPZOV. (*Ann. d. Physik*, No. 18, 1922.)—About a third of a century ago, when Hertz's demonstration of the actual existence of those electrical waves predicted by Maxwell, was still so recent that the wonder of it was still undulled by familiarity, it was no uncommon experience to meet in the periodical literature of physics some new proof that the new waves comported themselves in the same manner as light waves. Their reflection, refraction and interference were thus established. Then came the discovery of the X-rays and the battle between the conflicting views as to their nature. It is now known that they are light waves of extremely short length. For a long time it seemed impossible to reflect them from a surface. Now it is known that the surface of a crystal does this, and does it because within it are arranged layer after layer of atoms and electrons in regular order, though in fact diffraction is the real cause. This paper shows that the same effects are obtained when electrical waves enormous in comparison with X-rays are allowed to fall upon an artificial crystal. The elements are hollow copper cylinders, 12 mm. long and 3 mm. in diameter. Several of these are hung at equal intervals on a vertical thread. A sheet is formed by placing many such threads in the same plane and, finally, the crystal is made by placing several sheets parallel to one another and at equal distances. The electrical waves are of wave-length 3.5 cm. The cylinders act as resonators for the electrical waves.

When a bundle of electrical waves falls on the artificial crystal a reflected wave results and the intensity of this is measured as the crystal rotates, thus changing the angle of incidence. As the crystal turns the intensity of the reflected wave passes through maxima and minima, just as is the case with X-rays reflected from a natural crystal. More than this, when the positions of the crystal for maximum and minimum reflections are observed and the X-ray formula for the wave-length is applied, the result of the calculation is 3.2 cm. This may seem not sufficiently close to the value already given, 3.5 cm. When, however, the length of the waves was measured in the beam reflected from the crystal it was found to be 3.2 cm. Thus the two methods give concordant results. By some resonance effect the cylinders make the length of the reflected wave less than that of the incident wave.

The reflection was studied with one, then with two sheets and so on. The addition of the second sheet to the first caused a notable increase in the strength of the reflected ray, the third sheet produced a smaller increase and the presence of more sheets scarcely had any effect.

It is of interest that this very important work was done in the laboratory of the University of Moscow. G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

THE SO-CALLED HABITUATION TO "ARSENIC": VARIATION IN THE TOXICITY OF ARSENIOUS OXIDE.[1]

By Erich W. Schwartze.

[ABSTRACT.]

THE toxicity of undissolved arsenious oxide varies markedly according to the fineness of its subdivision. Slight differences in toxicity of dissolved arsenious oxide are observed in different species of animals. The proportional differences are not always found when undissolved arsenious oxide is used. The behavior of undissolved arsenious oxide in the alimentary canal appears to be superimposed upon the species reaction to the dissolved arsenious oxide. Chickens presumably convert a coarse preparation into a fine one in their gizzards, so that the differences between coarse and fine preparations are here less marked than those found in the mammals tested. These results correlate a mass of acute toxicological data which heretofore have led to controversy and apparently contradictory evidence. Large doses of certain preparations of undissolved arsenious oxide and sulphide were recovered practically intact by washing and sieving the fæces.

The literature upon the subject of habituation to "arsenic" has been reviewed in the light of the data secured by the Bureau of Chemistry. No unimpeachable evidence exists that either man or other higher animals can acquire a tolerance to this drug, owing chiefly to the erroneous assumption that all preparations of undissolved arsenious oxide possess equal potency, and approach in degree the potency of dissolved arsenious oxide. The consumption of large amounts of undissolved arsenious oxide can be as readily explained on the basis that a relatively insoluble and coarse preparation was used as by assuming that habituation had been produced. The toleration of large doses may therefore be due not to an attribute inherent in the consumer, but to an attribute inherent in the preparation used, namely, its relative insolubility due to the relatively small extent of exposed surface of the particles and the low specific rate of solution.

* Communicated by the Chief of the Bureau.

[1] Published in *J. Pharmacol.*, **20**, Oct., 1922, 181.

QUANTITATIVE DETERMINATION OF ANTHRAQUINONE.[2]

By O. A. Nelson and C. E. Senseman.

[ABSTRACT.]

A METHOD has been developed by which anthraquinone may be determined quantitatively in mixtures containing also phenanthraquinone, anthracene, phenanthrene, phthalic anhydride, phthalic acid, or other oxidation products of anthracene or phenanthrene. It consists essentially in reducing the anthraquinone to the red oxanthranol, using zinc powder and 5 per cent. solution of sodium hydroxide. The red solution is filtered in vacuum and titrated with standard potassium permanganate.

THE PREPARATION OF PHENYLGLYCINE-O-CARBOXYLIC ACID. I. FROM ANTHRANILIC ACID AND MONOCHLORACETIC ACID.[3]

By Herbert L. Haller.

[ABSTRACT.]

A STUDY of the preparation of phenylglycine-o-carboxylic acid from anthranilic acid and monochloracetic acid has been undertaken. Optimum conditions have been determined for (1) concentration in water of the reacting substances, (2) time allowed for reaction, (3) ratio of reacting materials, (4) condensing agent, and (5) temperature of reaction mixture.

Pure Ozone.—SEBASTIAN KARRER and OLIVER R. WULF (*Jour. Amer. Chem. Soc.*, 1922, xliv, 2391–2397) prepared pure ozone by the fractional distillation of oxygen, which had been ozonized, then liquefied. The molecular weight of the pure ozone was determined by a vapor density method and found to be 47.3. The fact that the molecular weight is slightly lower than 48 is attributed to the presence of a small amount of oxygen. J. S. H.

Pure Picric Acid.—STANLEY R. BENEDICT, of Cornell University Medical College (*Jour. Biol. Chem.*, 1922, liv, 239–241), describes the preparation of picric acid of a high degree of purity by recrystallization of the technical grade of commercial picric acid from hot benzene. Since the solution of picric acid in benzene is highly inflammable, electric heating apparatus is used. The product obtained by this process is so pure that it may be used as a reagent in certain colorimetric determinations, such as that of creatinine. J. S. H.

[2] Published in *J. Ind. Eng. Chem.*, 14, Oct., 1922, 956.

[3] Published in *J. Ind. Eng. Chem.*, 14, Nov., 1922, 1040.

NOTES FROM THE U. S. BUREAU OF MINES.*

THE PRODUCTION OF CARBON-BLACK FROM NATURAL GAS BY THE HIGH VOLTAGE ARC.

By J. J. Jakowsky.

THE legislation in many States against the present method of producing carbon-black by the incomplete combustion of natural gas, and the continually increasing demand for gas for other purposes, indicate that the supply of carbon-black may gradually be decreased and that new methods for its production, utilizing a greater percentage of the carbon in the gas should be developed. In the course of investigations of the effects on hydrocarbons of high voltage discharges, it was noted that under certain conditions natural gas could be decomposed and that carbon-black could be produced.

The effects of several types of electrical discharges on natural gas have, accordingly, been studied in order to find out the fundamental factors underlying the reactions and their possible influence in the recovery of a greater part of the carbon content of natural gas than is now possible. Present commercial plants using natural gas for the manufacture of carbon-black recover from 0.8 to 1.5 pounds of carbon-black per thousand cubic feet of gas consumed, or less than 5 per cent. of the total carbon in the gas. It should be noted, however, that the present methods involve heating the gas to incandescence by burning it as a luminous flame, and a considerable part of the gas is thus consumed as a source of heat. If this heat can be supplied from some other source, or if a more efficient method of applying the energy contained in part of the gas, to the decomposition of the rest of it, can be worked out, then a greater yield of carbon-black per thousand cubic feet of gas can be expected. Results showed that electrical production of carbon-black is a promising field, but further research is necessary to determine its commercial feasibility. Further details on the experiments are given in Serial No. 2417, recently published by the Bureau.

* Communicated by the Director.

GOLD IN OIL SHALES AND ITS POSSIBLE RECOVERY.

By Thomas Varley.

STATEMENTS have appeared in the technical press, indicating that valuable metals such as gold, silver, platinum, and other rare metals, have been found and also have been successfully extracted from oil shales. An investigation of the subject was made by the metallurgical division of the Bureau of Mines, in order, if possible, to determine to what extent, if any, metals of value do occur in oil shales, and if so, the feasibility of attempting their recovery by the processes said to have been used for that purpose. An agreement was entered into with the owner of an extensive oil shale deposit in Wyoming, whereby I personally collected the samples of shales for use in the investigation.

The samples tested contained minute amounts of gold, to the extent of possibly 40 or 50 cents per ton of original shale, but the amount found is not of commercial value.

No special precautions are necessary in assaying shale for gold, any direct assay by a reliable method will give the true gold content of the original material. Further details will be found in Serial No. 2413, recently published by the Bureau.

PREPARATION OF LIGHT ALUMINUM-COPPER CASTING ALLOYS.

By R. J. Anderson.

IN aluminum-alloy foundry practice, light aluminum-copper alloys are preferred for general use for castings, in fact, as far as can be estimated from the available figures, the domestic production of castings from an alloy containing approximately 92 per cent. of aluminum and 8 per cent. of copper was about 97 per cent. of the castings in all kinds of alloys in 1920, which amounted to about 81,000,000 pounds. Several other binary aluminum-copper alloys are employed for commercial castings; these contain from 2 to 13.5 per cent. of copper, the remainder being aluminum. In the United States, the alloy containing 92 : 8 aluminum is regarded as the best alloy available for general casting purposes and for some special castings. In addition, more or less definite light alloys have been developed for particular uses, notably piston and carburetor alloys and alloys for so-called leak-proof parts.

Aluminum-alloy foundries in the United States employ three methods for introducing copper into aluminum in making light aluminum-copper alloys: (1) The use of copper directly; (2) the use of 33:67 copper-aluminum alloy; and (3) the use of 50:50 copper-aluminum alloy. The usual method of preparing rich alloys is to melt the copper and part of the aluminum separately and then to pour the copper into the aluminum, keeping the temperature as low as possible by adding the remainder of the cold aluminum. Experiments of the Bureau of Mines in the preparation of the rich alloys and No. 12 alloy have yielded data with regard to dross losses, relative costs, and merits of methods. Further details will be found in Technical Paper 287, of the Bureau of Mines.

On the Selective Absorption of Electric Waves in Dielectrics. W. ROMANOFF. (*Ann. d. Physik*, No. 18, 1922.)—Whatever is related to the nexus between matter and radiation may throw light on the structure of matter. The most thorough investigation of radiation and absorption has been made for the wave-lengths of the visible spectrum and the adjacent fields of the infra-red and ultra-violet; the territory of the X-rays is now under examination. It is in the range of the electric waves that the greatest gap in our knowledge of this subject exists.

A very simple method is here presented for studying the absorption of electric waves by liquids. A train of waves is set up along two wires. About 4 milligrams of liquid in a tube of fused quartz is placed where experiment has shown that it will not unduly disturb the electrical relations of the system. As the liquid absorbs the waves its temperature rises. This is measured by a thermal junction. A second thermo-element measures the electrical energy falling on the liquid. The ratio of the energy absorbed to the energy incident characterizes the absorptive power of the liquid for the wave-length employed. This method gives only relative results but it has the merit of convenience. Several of the alcohols were thus investigated. In general for the range of wave-lengths applied, 570 to 880 mm., the absorption ratio grows less as the wave-length increases. In isobutyl alcohol the ratio has a maximum value at the wave-length of 600 mm. For ethyl alcohol the ratio is four times as great for a wave-length of 570 mm. as for one of 880 mm. Selective absorption is thus shown to exist in all the alcohols examined. G. F. S.

The German Dye Industry.—The leading nations involved against Germany were especially aroused during the war concerning the establishment of plants for manufacturing the synthetic coal-tar products, of which the dyes constitute the most important portion.

For many years Germany had practical control of the output of dyes, a condition due largely to the thorough coöperation of theory and practise, also to ingenious trade arrangements as to domestic distribution and export. The sudden stoppage of the supply became world-wide, for the Allies, of course, discontinued all commercial relations with their enemy, and the British blockade cut off supply to neutral countries. The several nations thus deprived proceeded to establish industries, and, after much difficulty and not a few failures, some of them have succeeded in producing many dyes and other synthetic tar products equal to those formerly manufactured only beyond the Rhine. Two methods have been employed as financial aids to these industries: Embargo on importation and high duty. Shortly after the Armistice, an embargo was placed by the U. S. Government on all dyes, except such as were not obtainable at reasonable price and satisfactory quality in the domestic market. This embargo has now been succeeded by the Tariff Act lately approved. The *Commerce Monthly* for December (issued by the National Bank of Commerce, New York) gives figures for the imports and domestic production of dyes, in pre-war and post-war years.

In 1914, the United States produced about six and one-half million pounds and imported nearly forty-six million pounds. In 1921, the figures are: Domestic production forty million pounds; importations somewhat less than four millions. In 1920, the domestic production was more than double that of 1921, but the result was large excess stock, which together with the industrial depression caused a material falling off in manufacture. It seems from the data at hand that the three great nations that were at war with Germany have succeeded in establishing satisfactory methods of making the more important dyes, but that these industries are still "infants" in the economic sense, and can only be maintained against German competition by embargo or tariff. Italy has employed the embargo method to prevent competition, but it has been for many years under German influence. The advertisements in Italian trade and scientific journals show that a very active propaganda is being carried on by German firms, and it will not be surprising if this newly developed industry is upset.

The problem is still more complicated by the fact there are large areas in which no such industry has been established, occupied by dense population who have demands for large amounts of dyes. Recent statistics show that Germany is now furnishing to China, Japan, Czechoslovakia, the Baltic States, and Austria large amounts of dyes. Germany's opportunities in some markets are materially increased by the monetary conditions. Since Germany's exchange is more nearly to the level of the exchanges of the markets of the Far East, the German manufacturer has an advantage over those in countries in which exchange is nearer par. All the data that come to us from Germany indicate that the Allied and Associated Powers have "scotched the snake, not killed it." H. L.

THE FRANKLIN INSTITUTE.

(*Proceedings of the Stated Meeting held Wednesday, December 20, 1922.*)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, December 20, 1922.

DR. WALTON CLARK, President, *in the Chair.*

The Board of Managers submitted its report. The report recorded the election to membership of:

Allen Addicks, Esq., B.S., Engineer, 106 South 36th Street, Philadelphia, Pennsylvania.

Francis L. Cramp, Esq., Assistant to President, Cramp's Shipyard, Philadelphia, Pennsylvania.

George C. Kuesel, Esq., D.D.S., Consulting Dental Surgeon, 1614 Locust Street, Philadelphia, Pennsylvania.

C. E. Kenneth Mees, Esq., D.Sc., Director, Research Laboratory, Eastman Kodak Company, Rochester, New York.

Joseph MacGregor Mitcheson, Esq., Assistant City Solicitor, 1018 Stock Exchange Building, Philadelphia, Pennsylvania.

Richard G. Sagebeer, Esq., B.A., Teacher, Haverford College, Haverford, Pennsylvania.

J. E. Shrader, Esq., Ph.D., Professor of Physics, Drexel Institute, Philadelphia, Pennsylvania.

Rodney H. True, Esq., Ph.D., Professor of Botany, University of Pennsylvania, Philadelphia, Pennsylvania.

William C. Tuttle, Esq., Manager of Trust Investments, Girard Trust Company, Broad and Chestnut Streets, Philadelphia, Pennsylvania.

Charles A. Williams, Esq., Chemist, 119 N. College Avenue, Oxford, Ohio; lectures before the Sections as follows:

"Recent Aeronautic Investigations and the Airplane Industry," by
Joseph S. Ames, Ph.D., LL.D.,
Professor of Physics,
The Johns Hopkins University,
Baltimore, Maryland;

"Recent Advances in Photographic Theory," by
C. E. Kenneth Mees, D.Sc., Director,
Research Laboratory,
Eastman Kodak Company,
Rochester, New York;

"The Earliest Apparatus and Procedures of Photography: Contributions to the Centenary of Modern Photographic Methods," by

Henry Leffmann, A.M., M.D.,
Lecturer on Research,
Philadelphia College of Pharmacy and Science,
Philadelphia, Pennsylvania;

and a lecture before the Stated Meeting November 15, 1922, by

E. Newton Harvey, Ph.D.,
Professor of Physiology,
Princeton University,
Princeton, New Jersey,

on "Animal Luminescence";

also additions to the library by gift, 83 volumes and 209 pamphlets; by purchase, 11 volumes and 1 pamphlet.

The Committee on Nominations appointed by Vice-President Henry Howson in accordance with a resolution passed at the Stated Meeting, held November fifteenth last, presented the following list of nominees to be voted for at the annual election to be held on Wednesday, January 17, 1923:

For President (to serve one year), Walton Clark.

For Vice-President (to serve three years), W. C. L. Eglin.

For Treasurer (to serve one year), Benjamin Franklin.

For Managers (to serve three years), Gellert Alleman, G. H. Clamer, Theobald F. Clark, Walton Forstall, Benjamin Franklin, Harry F. Keller, George D. Rosengarten, Wm. Chattin Wetherill; (to serve two years), J. T. Wallis; (to serve one year), J. Bartleman Klumpp.

On motion, duly seconded, the nominations were closed.

The Chairman then recognized Dr. Thomas D. Cope, who introduced Dr. A. H. Pfund of The Johns Hopkins University, Baltimore, Maryland, who had recently been awarded the Edward Longstreth Medal for his Cryptometer, Paint Film Gauge, Colorimeter and Rotating Sector.

Doctor Cope said, "Mr. President, Members of the Institute, Ladies and Gentlemen: Some time ago our medalist, Doctor Pfund, was called upon to apply in the paint industry the knowledge which he had acquired as a physicist while working upon the problems which he had met in his laboratory. He has left his mark upon the paint industry in the form of four instruments, the Cryptometer, the Paint Film Gauge, a Colorimeter for nearly white surfaces, and a Precision Rotating Sector. The Cryptometer is an instrument for determining the area which one gallon of white or black paint will conceal. The Paint Film Gauge permits a rapid determination of the thickness of a film of wet paint. The Colorimeter enables the deviation from true white of a nearly white surface to be determined both qualitatively and quantitatively. The Precision Rotating Sector enables the observer to determine the angular opening of a sector while the sector is in rapid rotation. The essential feature of this instrument is a simple and elegant optical device.

"These instruments have been thoroughly investigated by the Committee on Science and the Arts. They have been found sound in principle, well designed and well adapted to meet the problems which they are intended to solve. The Committee finds, too, that these instruments are in extensive use

and are looked upon by their users as important contributions to the art of precise measurement in the paint industry. In recognition of the originality and ingenuity displayed by Doctor Pfund in designing these instruments by means of which he has introduced physical methods of precision into the paint industry, the Institute acting on the recommendation of the Committee on Science and the Arts has awarded to him the Edward Longstreth Medal of Merit.

"I have the honour, Mr. President, to present to you Dr. A. H. Pfund, Associate Professor of Physics at Johns Hopkins University, Baltimore, Maryland."

The Chairman then presented the Medal, Certificate and Report to Doctor Pfund, who in accepting them said:

"*Mr. President:* This is an honor, indeed, to be thus recognized by The Franklin Institute. I accept this medal gratefully and in all humility.

"The work for which the present award was made lies in the field of applied science. It is often thought that this field is a borrower only—taking the ideas and discoveries of pure science and making them useful to man. This is a mistake. Practical things, be they products or processes, bring about new conditions which, in turn, unearth new problems. These problems, if pursued to their logical conclusion, inspire research of the purest and loftiest type.

"Thus is a reciprocity established which aids in the furtherance of both fields of endeavor."

The paper of the evening was then presented by Dr. W. F. G. Swann, Professor of Physics, University of Minnesota, Minneapolis, Minnesota, on "Unsolved Problems of Cosmical Physics." The status of our knowledge of the earth's magnetic and electric phenomena was discussed as well as the origins of magnetic storms, earth-currents, the aurora borealis and their relations to the sun's activity. Consideration was also given to the modern views of the origin of gravitation and the bearing of Einstein's theory upon gravitational phenomena. The subject was illustrated by lantern slides.

A unanimous vote of thanks was extended to the speaker.

Adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, December 6, 1922.)

HALL OF THE INSTITUTE,
PHILADELPHIA, December 6, 1922.

DR. JAMES BARNES *in the Chair.*

The following reports were presented for final action:

No. 2793: Cryptometer, Colorimeter, Paint Film Gauge and Rotating Sector. The Edward Longstreth Medal to Dr. A. H. Pfund of Baltimore, Maryland.

No. 2795: Johnson Hydraulic Valve. The Elliott Cresson Medal to Mr. Raymond D. Johnson of New York.

The following reports were presented for first reading:

No. 2801 and No. 2802 } The Franklin Medal.

R. B. OWENS,
Secretary.

SECTIONS.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, November 9, 1922, at eight o'clock, with Dr. Harry F. Keller in the Chair. The minutes of the previous meeting were read and approved.

Wilder D. Bancroft, Ph.D., World War Memorial Professor of Physical Chemistry in Cornell University, Ithaca, New York, presented a communication on "Structural Colors in Feathers." These conclusions were drawn: Reds, yellows and blacks are pigment colors; whites, blues, greens, and the metallic colors are structural colors; the metallic colors are interference colors, due to thin films.

The paper was discussed; a vote of thanks was extended to Doctor Bancroft; and the meeting adjourned.

JOSEPH S. HEPBURN,
Secretary.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, November 23, 1922, at eight o'clock, with Dr. Thomas D. Cope in the Chair. The minutes of the previous meeting were read and approved.

Joseph S. Ames, Ph.D., LL.D., Professor of Physics at The Johns Hopkins University and Director of the Office of Aeronautical Intelligence, National Advisory Committee for Aeronautics, presented a communication entitled, "Recent Aeronautic Investigations and the Airplane Industry." A description was given of (*a*) the distribution of forces over the various surfaces of an airplane, (*b*) the motion of the airplane in manœuvres, and (*c*) the study of the scale effect in aerodynamics. The immediate application of experimental researches in the airplane industry was discussed.

The communication was discussed; a vote of thanks was extended to Doctor Ames; and the meeting adjourned.

JOSEPH S. HEPBURN,
Secretary.

Section of Physics and Chemistry and Section of Photography and Microscopy.—A joint meeting of the Sections was held in the Hall of the Institute on Thursday evening, December 7, 1922, at eight o'clock, with Dr. H. J. M. Creighton in the Chair. The minutes of the previous meeting were approved as published.

C. E. Kenneth Mees, Sc.D., Director of the Research Laboratory, Eastman Kodak Company, Rochester, New York, delivered a lecture on "Recent Advances in Photographic Theory," in which a resumé was given of the recent researches in this field.

The lecture was illustrated by means of lantern slides. The communication was discussed; a vote of thanks was extended to Doctor Mees; and the meeting adjourned.

JOSEPH S. HEPBURN,
Secretary.

Section of Physics and Chemistry and Section of Photography and Microscopy.—A joint meeting of the Sections was held in the Hall of the Institute on Thursday evening, December 14, 1922, at eight o'clock, with Mr. Alfred Rigling in the Chair. The minutes of the previous meeting were read and approved.

Henry Leffmann, A.M., M.D., Ph.D., Lecturer on Research in the Philadelphia College of Pharmacy and Science, delivered a lecture on "The Earliest Apparatus and Procedures of Photography: Contributions to the Centenary of Modern Photographic Methods." The work of Niépce, and other investigators prior to Daguerre, concerning the action of light on various substances was reviewed; and the types of camera and the technic used by these early investigators were described. The lecture was illustrated by means of experiments and lantern slides.

The paper was discussed; a vote of thanks was extended to Doctor Leffmann; and the meeting adjourned.

JOSEPH S. HEPBURN,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, December 13, 1922.)

RESIDENT MEMBERS.

MR. FRANCIS L. CRAMP, Cramp's Shipyard, Richmond and Norris Streets, Philadelphia, Pennsylvania.

DR. GEORGE C. KUESEL, 1614 Locust Street, Philadelphia, Pennsylvania.

MR. JOSEPH MACGREGOR MITCHESON, 1018 Stock Exchange Building, Philadelphia, Pennsylvania.

MR. RICHARD G. SAGEBEER, Harverford College, Haverford, Pennsylvania.

DR. J. E. SHRADER, Drexel Institute, Philadelphia, Pennsylvania.

DR. RODNEY H. TRUE, Department of Botany, University of Pennsylvania, Philadelphia, Pennsylvania.

MR. WILLIAM C. TUTTLE, Girard Trust Company, Philadelphia, Pennsylvania.
MR. CHARLES A. WILLIAMS, 917 Madison Street, Chester, Pennsylvania.

NON-RESIDENT.

DR. C. E. K. MEES, Director, Research Laboratory, Eastman Kodak Company, Rochester, New York.

ASSOCIATE.

MR. ALLEN ADDICKS, 106 South 36th Street, Philadelphia, Pennsylvania.

CHANGES OF ADDRESS.

MR. WALTER ATLEE, 218 East Twentieth Street, Baltimore, Maryland.
MR. GEORGE W. BIRCH, JR., 19 Fairview Avenue, Highland Park, Pennsylvania.
MR. JOHN STUART EASON, 522 Merchants Bank Building, St. Paul, Minnesota.
MR. HERMAN LIVINGSTON, Richards Park, Somerville, New Jersey.
MR. JOHN C. TRAUTWINE, 3rd, Morton Avenue and Providence Road, Morton, Pennsylvania.
MR. H. R. VAN DEVENTER, Dubilier Condenser and Radio Corporation, 48 West Fourth Street, New York City, New York.
MR. J. M. WEISS, 210 West 110th Street, New York City, New York.

NECROLOGY.

John Forrest Kelly was born in Carrick-on-Suir, Ireland, March 28, 1859, and died at Pittsfield, Massachusetts, on October 15, 1922. He came to the United States when a boy and graduated from Stevens Institute of Technology in 1878 with the degree of Bachelor of Science, the degree of Doctor of Philosophy being conferred upon him three years later by the same institution. In 1879 he entered the Edison Laboratory as a chemist, and later joined the staff of the Western Electric Company. During the following twenty-five years he acted as technical advisor to many important electrical interests. More than ninety patents were granted to Doctor Kelly for devices used in the generation, distribution, transmission and measurement of electrical power and energy. In 1895, he founded the Tel-Electric Company. In 1910, on the recommendation of The Franklin Institute, the City of Philadelphia awarded him the John Scott Legacy Medal and Premium for his electric piano player. In recent years, Doctor Kelly had been interested in processes for the drying of food products.

Doctor Kelly was a member of the leading scientfiic and technical societys of the United States and Europe. He became a member of The Franklin Institute on April 12, 1913.

Mr. John E. Carter, 5356 Knox Street, Germantown, Philadelphia, Pennsylvania.

Rear Admiral John R. Edwards, Bristol, Rhode Island.

Mr. John Wanamaker, 1300 Market Street, Philadelphia, Pennsylvania.

LIBRARY NOTES.

PURCHASES.

ADVISORY COMMITTEE FOR AERONAUTICS.—Report of the Light Alloys Sub-committee. 1921.

CROSS, C. F., and DORÉE, C.—Researches on Cellulose, vol. 4, 1910–21. 1922.

GANSWINDT, A.—Dyeing Silk, Mixed Silk Fabrics and Artificial Silks. Tr. by Charles Salter. 1921.

MARTIN, T. C., and COLES, S. L.—Story of Electricity, vol. 2. 1922.

NATIONAL ASSOCIATION OF COTTON MANUFACTURERS.—Year Book and Manual. 1922.

Newcomen Society for the Study of the History of Engineering and Technology, Transactions, vol. 1, 1920–21. 1922.

Physical Society of London and the Optical Society.—Discussion on the Making of Reflecting Surfaces. No date.

PLIMMER, R. H. A.—Analyses and Energy Values of Foods. 1921.

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SABATIER, P.—Catalysis in Organic Chemistry. Tr. by E. Emmet Reid. 1922.

SMITS, A.—Theory of Allotropy. Tr. by J. Smeath Thomas. 1922.

STILLMAN, J. M.—Paracelsus. 1920.

TUTTLE, J. B.—Analysis of Rubber. 1922.

GIFTS.

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American Society of Heating and Ventilating Engineers, Year Book 1922. New York City, New York, 1922. (From the Society.)

Association of Iron and Steel Electrical Engineers, Proceedings, 1921. Pittsburgh, Pennsylvania, no date. (From the Association.)

Australasian Association for the Advancement of Science, Report of the Fifteenth Meeting, January, 1921. Melbourne, Australia, 1921. (From the Association.)

Barber Asphalt Company, The Last Analysis and the Wonderland of Trinidad. Philadelphia, Pennsylvania, 1922. (From the Company.)

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Bruntons, Splicing and Socketing of Wire Ropes. Musselburgh, Scotland, 1922. (From the Company.)

Calkins Company, Catalogue H, "Calkins" Specialties. Los Angeles, California, 1922. (From the Company.)

Cambridge and Paul Instrument Company, Limited, Lists of Instruments, Pyrometers and Thermometers Nos. 100, 157, 161, 164, 165, 190, 191, 194, and 195A. London, England, 1922. (From the Company.)

Canada Department of the Interior, Irrigation Series, Bulletin No. 6, Irrigation Practice and Water Requirements for Crops in Alberta. Ottawa. Canada, 1922. (From the Department.)

Canada Department of Mines, Talc and Soapstone in Canada by Hugh S. Spence. Ottawa, Canada, 1922. (From the Department.)

Canadian Car and Foundry Company, Limited, Bulletins Nos. T2 and S5. Montreal, Canada, 1921. (From the Company.)

Carborundum Company, Booklet of Carborundum Anti-slip Tile. Niagara Falls, New York, 1922. (From the Company.)

Climax Engineering Company, Bulletin 1001. Clinton, Iowa, 1922. (From the Company.)

Century Electric Company, Bulletins Nos. 28, 29, 30 and 31. St. Louis, Missouri, 1922. (From the Company.)

Coeur d'Alene Hardware and Foundry Company, Bulletin No. 21. Wallace, Idaho, 1922. (From the Company.)

Colorado State Bureau of Mines, Annual Report for the Year 1921. Denver, Colorado, 1922. (From the Bureau.)

Connecticut State Geological and Natural History Survey, Bulletins 23 to 32 inclusive. Hartford, Connecticut, 1920. (From the State Geologist.)

Connersville Blower Company, Bulletin No. 4, Rotary Displacement Meters. Connersville, Indiana, 1922. (From the Company.)

Consolidated Pneumatic Tool Company, Limited, Electric Tool Catalogue. London, England, 1922. (From the Company.)

Constantinesco, George, Theory of Wave Transmission and Pamphlet on Wave Transmission. London, England, 1922. (From Mr. Walter Haddon.)

Continental Radio and Electric Corporation, Modern Radio 1922. New York City, New York, 1922. (From the Corporation.)

Crouse-Hinds Company, Catalogue No. 2000, Condulets. Syracuse, New York, 1922. (From the Company.)

Cunard Steamship Company, Limited, Over Eighty Years of Trans-Atlantic Travel and Atlas of the World. New York City, New York, 1922. (From the Company.)

Dayton-Dowd Company, Booklet on Centrifugal Pumps. Quincy, Illinois, 1922. (From the Company.)

Dixon Valve and Coupling Company, Catalogue No. 6. Philadelphia, Pennsylvania, 1922. (From the Company.)

Dust Recovering and Conveying Company, Bulletin No. 5. Cleveland, Ohio, 1922. (From the Company.)

Electric Storage Battery Company, Binder containing a Complete Set of Bulletins, Form 1296 and two booklets "Facts." Philadelphia, Pennsylvania, 1922. (From the Company.)

Engineer Company, Turner Baffle Book. New York City, New York, 1922. (From the Company.)

Falk Corporation, Bulletins Nos. 31 and 32, Herringbone Gears. Milwaukee, Wisconsin, 1922. (From the Corporation.)

Fall River Water Works, Report of the Watuppa Water Board. Fall River, Massachusetts, 1922. (From the Works.)

Federal Telephone and Telegraph Company, Bulletin No. 119-W. Buffalo, New York, 1922. (From the Company.)

Georgetown University, Triennial Report of the Extra-curriculum Activities of Georgetown University. Washington, District of Columbia, 1922. (From the University.)

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Goodall Rubber Company, Incorporated, Rubber Products and Semi-Metallic Hose. Philadelphia, Pennsylvania, 1922. (From the Company.)

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BOOK NOTICES.

CATALYSIS IN ORGANIC CHEMISTRY. By Paul Sabatier, Member of the Institute. Translated by E. Emmet Reid, Johns Hopkins University. xxiv-969 pages, pages with name and subject indexes, 8vo. New York, D. Van Nostrand Company. Price, $5 net.

The term catalysis in its chemical application was introduced by Berzelius, but was in use in English, at least, as early as 1635, with the general meaning of catastrophe or dissolution. It was also used by Libavius.

Berzelius' application of it was first made in an article in the *Ann. d. Chim.* (1836, vol. 61, 156), in which he expressed his view as follows:

"This new force, which was unknown until now, is common to organic and inorganic nature. I do not think that it is a force wholly independent of the electrochemical affinities of matter; on the contrary, I think that it is only a new manifestation, but in so far as we can note the connection between them and their mutual relations, it will be appropriate to designate it by a distinct name. I will call it *catalytic force*, and will term *catalysis* the decomposition of substance by this force, analogous to our use of the term analysis for the decomposition of substances by chemical affinity."

It is interesting to note that four years before Berzelius published his paper, Döbereiner had discovered a striking instance of catalysis in the inorganic field, without, however, discussing the nature of action or assigning any title to it. This was the action of manganese dioxide in facilitating the decomposition of potassium chlorate. His report appeared in *Annalen* (1832, I, 236). It is a little surprising that the earliest use of the term catalysis by Berzelius is in Sabatier's work referred to his *Traité de Chimie* of 1845, whereas the date of his application of the term is, as noted above, nine years earlier.

Catalytic actions have been extensively studied and an immense number of instances is known. Many are of only theoretical interest, but many others again are of the greatest practical importance. The mechanism of the action is still in great measure obscure. Even the exact limitations of the phenomena are not absolutely fixed. Ostwald's definition has been in favor. It is "a catalyst is a substance which influences the velocity of a reaction without appearing in the final product." This would, as Sabatier remarks, greatly widen the extension of the term, for water has a very active power of increasing the velocity of reactions. The degree of fineness of powders is also influential. Strictly speaking the catalyst does appear in the final product, although not as part of the results of its action. Perhaps a better, though slightly more pedantic, definition is "a substance that modifies the specific velocity of a reaction without stoichiometric participation therein." The work in hand devotes considerable space to the mechanism of catalysis. A very interesting phase of the subject is the susceptibility of catalysts to interference by the presence of small amounts of other substances and also susceptibility to temperature and hydrogen-ion concentration. These latter influences have been especially noted in regard to the class of catalysts commonly termed "enzyms" or "non-organized ferments," the latter, however, a phrase that should be avoided. Diatase, invertase, pepsase, trypsase and similar catalysts, that take such a great part in the processes of digestion in plants and animals, are very susceptible to temperature and to the reaction of the liquid. The susceptibility of many catalysts to interference by small amounts of other substances, generally called "poisoning," has been studied a great deal in connection with some industrial process. Thus, the contact method for sulphuric acid depends on the use of platinum in a finely divided condition, but the presence of some other metals, such as arsenic and mercury in very minute amounts, will soon render the platinum inert. Berliner has shown that the presence of fatty vapors in the air, or grease from the stops,

will decrease the absorption of hydrogen by palladium to practically zero. In this connection the work of Chaney, presented to the thirty-ninth general meeting of the American Electrochemical Society (1919) on the activation of charcoals, will be of value. It was shown that all primary amorphous carbon consists essentially of a stabilized complex of hydrocarbons adsorbed on a base of active carbon. Charcoals prepared at moderately high temperatures retain considerable amounts of hydrocarbons. A hydrocarbon resembling anthracene, boiling at 360° C., was isolated from cedar charcoal which had been calcined at 850° C., and chlorine substitutions may be obtained in notable quantity by passing chlorine over coconut or other charcoals which have been calcined at high temperatures.

As might be expected, a large space in the book is devoted to the procedures of hydrogenation, a field in which the author has been very actively engaged and in which he has been a pioneer. Outside of the chapters on hydrogenation, a large amount of data of various types is to be found, and the book shows how extensive and complicated is the field of catalytic action. Being limited to organic chemistry, many phases of the phenomenon are necessarily omitted, but it seems that the process for production of ammonia by direct union should have been included. It is true that the main object of the process as applied practically is to the manufacture of inorganic bodies, but ammonia and nitric acid have intimate relations with organic chemistry, and the Haber process has been so much discussed lately that it would have been interesting and useful to have the opinions of the author and translator concerning it, and concerning the cause of the terrific explosion at the Oppau plant. The translator has done well in the work of turning the French into English, and has also done an especial service in verifying the numerous references. We must also thank him cordially for having given two very full indexes—names and subjects—which were probably lacking in the original, as French scientists are notoriously and criminally negligent on that score. One point in the make-up of the book deserves unfavorable criticism. The text is divided into many brief paragraphs, and the index references are to these paragraphs. This, in itself, is not seriously objectionable, but the paging of the book is carried on the inside of each leaf, while the initial and final paragraph numbers are in the places usually occupied by the paging. There seems to be no necessity for this arrangement. It is certainly very unusual in American books, and it is to be hoped that the custom will not be followed. If the form is borrowed from the French original then we can say that there are some things which are not "ordered better in France."

HENRY LEFFMANN.

THE NEWCOMEN SOCIETY FOR THE STUDY OF THE HISTORY OF ENGINEERING AND TECHNOLOGY. Transactions, Vol. I, 1920–21. 77 pages, official data and index, 18 plates, quarto form, 7½ by 10 in. Printed for the Society. Price 20 shillings.

The scope of the society is sufficiently indicated in its title. Although at present made up of British membership, it will be the endeavor of its promoters to make it international. It is believed to be the first society formed for its purpose. The plates are representations of early British inventions.

The initial article is by E. W. Hulme, B.A., entitled "An Introduction to the Literature of Historical Engineering to the Year 1640." It would seem to be better form to say "Historical Literature of Engineering," which is really what the author means, but this may be thought hypercriticism. The history of engineering, it appears, has its mysteries, for an article by L. St. L. Pendred is on "The Mystery of Trevithik's London Locomotives." The formation of the society and the appearance of the first volume of its Transactions are gratifying evidences of the spread of a broader culture among those whose labors are so strongly directed to the practical side of human affairs. Full information as to the terms and conditions of membership can be obtained by addressing the Hon. Secretary and Treasurer, H. W. Dickinson, M.I., Mech.E., The Science Museum, South Kensington, London, S. W. 7.

HENRY LEFFMANN.

THE PROPERTIES OF ELECTRICAL CONDUCTING SYSTEMS, INCLUDING ELECTROLYTES AND METALS. By Charles A. Kraus, Clark University. 408 pages, indexes and 70 illustrations, 8vo. New York, The Chemical Catalog Company, 1922. Price $4.50 net.

This is another volume of the American Chemical Society's monograph series, and in form and style follows those previously issued. The series is intended to present special considerations of chemistry and physical chemistry, in a detail that is not possible in the ordinary text-book or dictionary. The volume in hand goes very deeply into the theories and practise of electrolysis, though not dealing directly with technologic phases. The enormous development of electricity in all fields is evident in many ways, and in this book we have the evidence of how vast has been the advance since Faraday announced his results on electrolytic effects. Professor Kraus states in the preface that the most recent developments of chemistry and molecular physics have been principally along the line of the application of the theory of ionization to our conception of matter. The primary views have passed away, as is the case with all early theories, but have served as a guide in directing and suggesting research. To-day an intimate relation between matter and electricity is accepted as a principle as securely established as the atomic theory itself. The theoretical interest and practical importance of electrolytic phenomena have been a powerful impulse towards experimenting along such lines, and hence the literature of chemistry and physics abounds with contributions purely theoretical and purely practical, as well as those which touch both fields. The successful establishment of the Amerian Electrochemical Society is one of the indications of the extensive cultivation of this branch of science. The data that have been obtained by the many workers are scattered through many journals and transactions, and the purpose of the present volume is to summarize these contributions and thus make them easily available to the student or to research workers. The volume is also adapted to the wants of workers in allied branches.

Principal attention has been given to systems in which ionic phenomena are clearly in evidence. Metallic systems are included, as a relation between phenomena in metallic and electrolytic systems is unmistakeable. The subject of electrolytic solutions is the most extensively treated, and all data are

given from essentially an empirical standpoint, as the author holds that as yet an adequate theory of electrolytic solutions has not been brought forward. The theory finally adopted will, he thinks, be a composite and will embody some of the fundamental elements of the older ionic theory.

Many tables and diagrams are added, and the book constitutes a very comprehensive collection of data on a subject of great importance and much abstruseness. The numerous references to the literature enable the user of the book to fill out details along any line that may be in hand. The mechanical execution is excellent. HENRY LEFFMANN.

THE RECOVERY OF VOLATILE SOLVENTS. By Clark Shove Robinson, Massachusetts Institute of Technology. 183 pages, index and 73 illustrations. 8vo. New York, The Chemical Catalog Company. Price $2.50 net.

The term volatile solvents might be difficult to define, for water and mercury come within a broad interpretation thereof. The book in hand, of course, does not cover so wide a range, but relates to the familiar organic liquids that are used for extractions with substances that water does not appreciably dissolve. In the analytic laboratory the use of "miscible" and "immiscible" solvents is frequent, and here again a captious critic might challenge the accuracy of the phrase, for in strict construction, every so-called immiscible solvent dissolves to a certain extent in the other liquid—almost always water—and is also to a limited extent dissolved by it. The author gives, indeed, a rather wide interpretation to his title, but not in either of the directions just noted, descriptions being given of methods used for extracting gasoline from natural gas.

The recovery of volatile solvents has been long practised on a limited scale in the analytic and research laboratory, especially with the more expensive liquids, but the purpose of this work is to give the existing state of the art and theories as applied to large scale operations. The solvents used in the laboratory and even in industries in early days were few. Alcohol, ether, chloroform, light petroleum and light tar distillates were the familiar forms. The list in this book includes over two score substances, some of them moderately complicated synthetic products. The importance of accurate study of the physics and chemistry of solvent recovery lies principally in the cost of the material, but in some cases increasing scarcity is a dominant urge. Notwithstanding the fact that the present work is the first of its type that has appeared, the literature of the subject is very extensive. It is presented in excellent form in an appendix, the items being arranged chronologically. A considerable number of the items are records of patents, a fact that indicates the extensive development that the procedures have in industries. Scientists should interest themselves in securing some international and authoritative methods of quoting and arranging references. Two methods of arranging are in frequent use: Chronological and alphabetical, the latter by authors' names. Neither method is really commendable. A classification by subject, even in a special bibliography, would be the proper method, but the work of making such a list is laborious and costly. In addition to deciding on the arrangement, a precise method of quoting each reference should be used. In quoting from a periodical that has both volume and year, both should be given, as one datum serves as check upon possible error in the other. The

bibliography in the book in hand offends a great deal in this respect, the volume being rarely quoted. In many cases a supplementary reference to C. A. is given, with both volume and year. A commendable feature is the use of Arabic numerals for the volume number. The practise of employing Roman numerals for volume numbers is a relic of the middle ages that may well be eliminated in science. The higher numbers are difficult to read and typographic errors are far more likely to occur than with the common figures. An instance of the viciousness of the Roman numeral system came recently to the notice of the writer of this review. A reference was given to *Gilb. Ann.*, iv. It happened that from another source the reference was known to be "lv." It can be seen what a wild goose chase the searcher would have undertaken if the first reference had been the only one at hand. The addition of the year would, of course, have sooner or later put him on the right track, hence the advisability of giving both data. In many cases journals of long standing have been issued in series, and with all such the series should of course be given. It is evident, however, that in the case just mentioned, while iv and lv may be easily confused 4 and 55 can not be.

Turning to the contents of the book in hand, it is found that the subject is presented in much detail and very thoroughly. As the processes discussed are all mechanical at base, many illustrations of apparatus are given. The large number of quotations from patent-literature given in the bibliography will be of great aid to those in charge of recovery plants, who may have developed improvements on existing apparatus and desire to protect their inventions. Brief statements of the important points in many patents are appended to the reference. The author remarks that he has been much surprised to find that many devices that he believed to be new have been long anticipated. His experience in this direction is a common one. Scarcely any process of recent development is without anticipation in some degree. His experiences lead him to the view that so far as regards the basic processes of recovery there is very little opportunity for inventors, but this may be a rash prediction. The "patient search and vigil long" of the inventor is often unexpectedly rewarded. The physical chemistry of the procedures is taken up, and many tables and graphs are given to illustrate and explain the principles involved. The work constitutes a very valuable addition to the literature of chemical engineering, which has developed so extensively of late years in this country, a development that is steadily tending to render the nation independent of others. The mechanical construction of the book is of the excellent type which characterize the productions of the well-known publishing house. The literary style is not of the best. In the general text, which is largely descriptive and formally scientific, this does appear, but the preface is written in a weak style, with an over-use of words. Laxity of literary form seems to be the tendency in American scientific literature. The education of the student in science courses is directed so strongly to the practical side that training in the proper use of words and even in the proper method of speaking is being neglected. Probably the discontinuance of classical study has had something to do with this falling off. However, the merits of this book are in the material presented, and this criticism is merely a personal reaction of the reviewer to some of the setting.

HENRY LEFFMANN.

PUBLICATIONS RECEIVED.

The Analysis of Rubber, by John B. Tuttle, American Chemical Society Monograph Series. 155 pages, 8vo. New York, The Chemical Catalog Company, Inc., 1922. Price $2.50.

Catalysis in Organic Chemistry, by Paul Sabatier. Translated by E. Emmet Reid. 406 pages, 8vo. New York, D. Van Nostrand Company, 1922. Price $5.00.

Les Applications Élémentaires des Fonctions Hyperboliques a la Science de l'Ingénieur Electricien, par A. E. Kennelly, Professeur d'électricité appliquée, Université de Harvard. 153 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 15 Francs.

A First Book in Chemistry, by Robert H. Bradbury, A.M., Ph.D., Head of the Department of Science, South Philadelphia High School. 687 pages, illustrations, 8vo. New York, John Wiley and Sons, Inc., 1922. Price $5.00.

Introduction a la Théorie de la Relativité Calcul Différentiel Absoln et Géométrie, par H. Galbrun, Docteur es Sciences. 457 pages, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price 60 Francs.

La Composition de Mathématiques dans l'examen d'admission a l'École Polytechnique de 1901 a 1921, par F. Michel, M. Potron. Exercises d'application du cours de mathématiques spéciales. 452 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 40 Francs.

Théorie des Nombres, par M. Kraïtchik avec une préface de M. d'Ocagne. 229 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 25 Francs.

The Recovery of Volatile Solvents, by Clark Shove Robinson. First edition. 188 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1922. Price $2.50.

Belt Conveyors and Belt Elevators, by Frederic V. Hetzel, M.E. 333 pages, illustrations, 12mo. New York, D. Appleton and Company, 1922.

Le Tunnel du Simplon. Sa construction, son achèvement, 1898–1921. En commemoration de la pose de la dernière clef de voûte 4 Decembre, 1921. 47 pages, illustrations, plates, 8vo.

The Sanitation of Bath Houses, by Wm. Paul Gerhard, C.E. Reprinted from "Architecture and Building." 16 pages, illustrations, quarto. New York, Author, 1922. Price 60 cents.

National Advisory Committee for Aeronautics: Technical Notes No. 117, The Synchronization of N.A.C.A. Flight Records, by W. G. Brown. 3 pages, illustrations, photograph, quarto. No. 118, F-5-L Boat Seaplane-Performance Characteristics, by Lieutenant W. S. Diehl. 8 pages, illustrations, quarto. No. 119, The Elimination of Dead Centre in the Control of Airplanes with Thick Sections, by Thomas Carroll. 3 pages, illustrations, quarto. No. 120, A Preliminary Study of Airplane Performance, by F. H. Norton and W. G. Brown. 7 pages, illustrations, photograph, quarto. Eighth Annual Report, 1922. Administrative report without technical reports. 52 pages, quarto. Washington, Government Printing Office, 1922.

CURRENT TOPICS.

The Protection of Brass Weights. J. J. MANLES. (*Phil. Mag.*, Nov., 1922.)—Regular use in the laboratory for sixteen years and numerous re-standardizations have shown that Faraday's method of protecting iron weights is applicable also to weights of brass. The polished weights were heated in a semi-luminous gas flame until they were almost red hot and then were plunged at once into boiled linseed oil, where they remained to cool. After removal they were washed in turpentine and rubbed with old linen. The surface thus acquired a uniform tint of bronze. Recently the repetition of this treatment led to unsatisfactory results, attributed to a change in the chemical composition of the gas used for heating the weights. The following plan was adopted with success. The weight, evenly covered with linseed, was supported upon a few sharp points within a crucible which was then heated in a Bunsen flame. When the weight assumed a golden color the process was complete. After it had cooled in the crucible, the weight was rubbed with an old silk handkerchief and subsequently adjusted. The mass of the layer covering the surface was calculated to be about .00005 grm. per sq. cm.

G. F. S.

Early Chemical Industry in America is described by C. A. BROWNE (*Jour. Ind. Eng. Chem.*, 1922, xiv, 1066–1071). The Indians imparted to the first settlers a knowledge of rubber, maple sugar, chocolate, vanilla, cochineal, tapioca starch, and other commodities. The Spanish settlers devised the cold amalgamation or patio process for the extraction of silver from its ores; they and the French smelted the lead ores of Missouri in a crude fashion. The English introduced chemical manufactures. In 1642 the General Court of Massachusetts took measures to insure the manufacture of saltpetre. This compound was manufactured during the War of 1812 from wood ashes and the calcium nitrate deposits of the Mammoth cave.

J. S. H.

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